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SYNTHESIS OF SOME ORGANOMETALLIC AND COORDINATION COMPLEXES OF LANTHANIDE ELEMENTS. PART I. MIXED SANDWICH COMPLEXES. PART II. POLY(PYRAZOL-1-YL)BORATE COMPLEXES.

by

© ALBERT P. MASINO

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
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FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

IN

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled SYNTHESIS OF SOME ORGANOMETALLIC AND COORDINATION COMPLEXES OF LANTHANIDE ELEMENTS. PART I. MIXED SANDWICH COMPLEXES. PART II. POLY(PYRAZOL-1-YL)BORATE COMPLEXES submitted by Albert P. Masino in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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TO SUSAN

Abstract

Mixed sandwich complexes containing both the cyclopentadienide and cyclooctatetraenide moieties have been obtained for a variety of lanthanide metals. Difficulties were encountered in the syntheses, and these were, in part, attributed to the formation of the dinuclar complexes, $M_2(C_8H_8)_3$. The $(C_5H_5)M(C_8H_8)$ complexes, when isolated from tetrahydrofuran contain a coordinated THF molecule; thus giving evidence for the Lewis acidic character of the mixed sandwich complexes. This behavior has been investigated and adducts with cyclohexylisocyanide, pyridine, ammonia, and 1,10-phenanthroline have been isolated. The mixed sandwich complexes have been shown to be weaker Lewis acids than the corresponding $M(C_5H_5)_3$ derivatives and this has been attributed to the presence of the more reducing cyclooctatetraenide moiety. The infrared and NMR spectral data of the complexes indicate pentahapto and octahapto bonding modes of the carbocyclic rings, although additional interactions through solid state aggregation in the base free compounds cannot be ruled out. The spectral data suggest a greater interaction between the lanthanide ion and the C_8H_8 ring than with the C_5H_5 moiety. The chemical and spectral data show that the mixed sandwich compounds are highly ionic relative to related actinide derivatives. However, the observation of ring-metal skeletal vibrations in the Raman

spectra, charge transfer bands tailing into the visible region, and metal-ring coupling in the ^{13}C NMR spectrum of the Y complex seem to indicate that some covalency does exist in the bonding of these complexes.

The synthesis of hydrotris(pyrazol-1-yl)borate, $HBpz_3^-$, complexes has been extended to the lanthanide metals. The air stable $M(HBpz_3)_3$ derivatives and the hygroscopic $(HBpz_3)_nMCl_{3-n}\cdot xTHF$ complexes have been obtained. The infrared spectral data of the tris complexes indicate the presence of two solid state structural classes, one for compounds with the early and the other for the late lanthanide metals. It was postulated that the eight coordinate structure found for the Yb complex represents the prototype for the structure of the late lanthanide derivatives. The structure of the early members awaits X-ray analysis. The ^1H NMR spectra of the chloro derivatives were taken to indicate symmetrical tridentate bonding of the $HBpz_3$ moiety. The synthesis of organolanthanide derivatives containing the $HBpz_3$ fragment met with limited success. Although $(HBpz_3)M(C_8H_8)$ complexes could be isolated, σ-bonded compounds were not obtained.

The synthesis of $M(N^ipr_2)_3$ derivatives was attempted and with Pr a reasonably pure complex which also contained coordinated THF could be isolated. The utilization of these diisopropylamides as starting materials for the synthesis of other lanthanide complexes has been thwarted by their delicate nature.

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ABBREVIATIONS

Me - methyl, CH_3

TMS - tetramethylsilane, $Si(CH_3)_4$

Cp - cyclopentadienide, C_5H_5

1,10-phen - 1,10-phenanthroline, $C_{12}H_8N_2$

py-d_5 - pyridine-d_5, C_5D_5N

py - pyridine, C_5H_5N

THF - tetrahydrofuran, C_4H_8O

^{i}pr - isopropyl, $-CH(CH_3)_2$

PART I

CHAPTER ONE

INTRODUCTION TO ORGANOLANTHANIDE CHEMISTRY

1. General Consideration

The lanthanides are the fourteen elements following lanthanum in the Periodic Table in which the 4f orbitals become progressively filled upon proceeding from cerium to lutetium. These elements form the longest continuous series of chemically similar elements in the Periodic Table. Lanthanum, although strictly not a lanthanide, is a prototype for the chemical behavior of these elements. Thus the term lanthanide is often taken to include lanthanum itself.

The chemistry of these elements is predominantly ionic, and is essentially that of the 3+ oxidation state.* It is governed primarily by the size of the tripositive ions.[1,2,3] The ionic radii of scandium, yttrium, and the lanthanide metals are collected in Table 1. These radii show that yttrium, which lies above lanthanum in Transition Group III, can operationally be included to advantage in the discussion of lanthanide chemistry.

---

*Although the 2+ and 4+ species are also known, the most stable ions being those which thus attain the $f^{\circ}(Ce^{4+})$, $f^7(Eu^{2+}, Tb^{4+})$ and $f^{14}(Yb^{2+})$ configurations.

Table 1. Electronic Configuration and Radii for the Tripositive Ions

Element	Symbol	Electronic Configuration M^{3+}	M^{3+} Ionic Radii[a,b]	
			CN 6	CN 8
Scandium	Sc	[Ar]	.745	.870
Yttrium	Y	[Kr]	.900	1.019
Lanthanum	La	[Xe]	1.032	1.160
Cerium	Ce	$4f^1$[c]	1.01	1.143
Praseodymium	Pr	$4f^2$	.99	1.126
Neodymium	Nd	$4f^3$	.983	1.109
Promethium	Pm	$4f^4$	.97	1.093
Samarium	Sm	$4f^5$	.958	1.079 (1.27)[d]
Europium	Eu	$4f^6$	.947 (1.17)[d]	1.066 (1.25)[d]
Gadolinium	Gd	$4f^7$	.938	1.053
Terbium	Tb	$4f^8$	.923	1.040
Dysprosium	Dy	$4f^9$	.912	1.027
Holmium	Ho	$4f^{10}$	.901	1.015
Erbium	Er	$4f^{11}$	.890	1.004
Thulium	Tm	$4f^{12}$	.880	.994
Ytterbium	Yb	$4f^{13}$	.868 (1.02)[d]	.985 (1.14)[d]
Lutetium	Lu	$4f^{14}$	.861	.977

---

[a] Reference 4.

[b] Values for coordination numbers six and eight; CN 6 and CN 8 respectively.

[c] Only those electrons outside the closed rare gas shell are indicated.

[d] Radii for M^{2+} ions.

Scandium however, by virtue of its smaller size, has chemistry sufficiently different that its inclusion in the present synopsis is not warranted. Thus the term lanthanide, as used in this thesis, will be allowed to encompass the elements lanthanum to lutetium and what is said concerning the lanthanides will be understood to apply to yttrium as well unless this element is specifically excluded.

The initial investigations of the chemistry of the lanthanides dealt with the study of the coordination of the tripositive ions particularly with ligands of high electronegativity.[3,5] Two immediate observations were made: (i) the complexes possessed high coordination numbers (greater than six); (ii) the 4f orbitals were not substantially involved in the bonding to the ligands. The lack of 4f orbital involvement was attributed to the shielding effect of the completed $5s^2 5p^6$ octet which prevents strong metal-ligand interaction. The unavailability of the 4f orbitals and the relatively large size of the tripositive ions are two factors which have been said to account for the largely electrostatic character of the bonding as determined from magnetic and spectral data, and ligand lability.[1,6,7]

A general comparison between the bonding and the coordination properties of the lanthanide and 3d transition metal ions, taken from reference 3, is given in

Table 2. A substantial difference is immediately apparent. This is particularly true in reference to the use of the partly filled valence shell orbitals, which for the d-transition series generally are involved in strong metal-ligand interactions. The geometry of the complex results from the directional properties of the bonding which helps to maximize this interaction. On the other hand, for the lanthanide ions the coordination number and configuration around the metal are mainly the result of a balance between non-directional electrostatic forces.[1,6,9] A property of the lanthanides which influences both coordination number and geometry is the shrinkage of the ionic radii as the 4f orbitals are filled. This "lanthanide contraction", as it is commonly referred to, is a result of the imperfect shielding from the nuclear charge of one f electron by another f electron. Thus as the ionic size decreases the repulsion between ligands in the coordination sphere increases and the coordination of the lanthanide ion sometimes decreases as one proceeds across the series. In the case of yttrium coordination numbers of 7, 8, and 9 are equally common.

Although the involvement of the 4f orbitals in bonding of the lanthanides is small compared to the role of d-orbitals for transition metal ions, nevertheless, it may be that the f-electrons play a subtle part

Table 2. General Comparison of 4f-3d Metal Ions[a]

	Lanthanide Ions	Transition Metal Ions
Metal orbitals	4f	3d
Ionic radii	1.06-0.85 Å	0.75-0.6 Å
Common coordination numbers	6,7,8,9	4,6
Typical coordination Polyhedra	Trigonal prism Square antiprism Dodecahedron	Square Planar Tetrahedron Octahedron
Bonding	No metal-ligand orbital interaction	Strong metal-ligand orbital interaction
Bond direction	Little preference in bond directions	Strong direction bonding
Bond strength	Ligands bond in order of electronegativity F^-, OH^-, H_2O, NO_3^-, Cl^-	Bond strengths determined by orbital interaction normally in the following order CN^-, NH_3, H_2O, OH^-, F^-
Solution Complexes	Ionic rapid ligand exchange	Often covalent; covalent complexes normally exchange slowly

[a] Taken from Ref. 3.

in determining some of the chemical and physical properties of the lanthanide complexes. Studies involving complexes of the lanthanides can be used to expand the basic understanding of the chemistry of this series and to provide a comparative basis for the lanthanide (4f) and actinide (5f) series. It is for the latter series that more extensive involvement of f-orbitals in bonding is expected primarily due to the increased radial extent of the 5f- as compared to that of the 4f-orbitals.[8]

2. Organometallic Compounds

The preceeding paragraphs do not constitute an exhaustive survey of the bonding in lanthanide complexes, but they do indicate the prevalent feelings at the time of the initial syntheses of organometallic complexes of the lanthanides. As will be seen, certain researchers will slightly modify these bonding ideas, but the main conclusion that the bonding in organolanthanide complexes is primarily ionic remains.[10,11]

The organometallic chemistry of the lanthanides is an area of renewed and active interest,[10,12-14] with both π- and σ-complexes being reported. Since the area has been well reviewed,[10,12] only the more salient features will be mentioned below to give an historical perspective and to lead into the more recent developments. Major emphasis will be given to the cyclopentadienide and cyclooctatetraenide derivatives.

i) Cyclopentadienide Complexes.

The synthetic development of π-carbocyclic complexes began with the preparation by Birmingham and Wilkinson of the tricyclopentadienide complexes of the lanthanides,[15a] $M(C_5H_5)_3$ (M = La, Ce, Pr, Nd, Sm, Gd, Y) in 1954. This was followed by their report in 1956[15b] which extended the synthesis to M = Dy, Er, and Yb. The compounds were prepared by reacting the anhydrous metal halides with sodium cyclopentadienide in dry, oxygen free tetrahydrofuran as solvent and isolated by vacuum sublimation. These authors interpreted such properties as the extreme air and water sensitivity, the quantitative reaction of the $M(C_5H_5)_3$ complexes with iron(II) chloride to yield ferrocene $Fe(C_5H_5)_2$, the invariance of the effective magnetic moment with temperature and its closeness to the values for rare earth ions in other compounds (including aquo ions), and the similarity of the absorption spectra in tetrahydrofuran to those of the "free lanthanide ions" in aqueous solution to indicate that the metal ring interaction is electrostatic in nature.

No further synthetic reports appeared until 1963 when Dubeck *et al.* prepared the $(C_5H_5)_2MCl$ [16] and $(C_5H_5)MCl_2 \cdot 3THF$ [17] complexes, where M represents a lanthanide from samarium to lutetium. The procedure was similar to that of Birmingham and Wilkinson[15] with the former compounds isolated by sublimation and the latter by crystallization. The chemical and physical properties of these compounds are similar to the $M(C_5H_5)_3$ complexes, and the conclusion that the bonding is highly ionic was again reached. In their attempts to isolate chlorocyclopentadienide type compounds with earlier lanthanides than samarium only tricyclopentadienides could be detected. Dubeck has attributed this to some subtle effect of the lanthanide contraction.[2] This seems to be a reasonable assumption when coupled to the previously mentioned desire for high coordination numbers especially among the early lanthanides. The picture that seems to be emerging is that the chemistry of the organolanthanides is again significantly different from that of the d-transition series cyclopentadienyls,[18] and that the size of the metal ions plays a significant role in determining the synthetically available complexes.

Completing the syntheses of the cyclopentadienide derivatives were the reports by Fischer and Fischer[19] on $M(C_5H_5)_3$ (M = Tb, Ho, Tm, Lu); Manastyrskyj and Dubeck[20] on $Eu(C_5H_5)_3 \cdot THF$; Tsutsui[21] *et al.* on $Eu(C_5H_5)_3$; Okamoto[22] *et al.* on $(C_5H_5)_2YCl$; and Ibanez[23] on $(C_5H_5)_2MCl \cdot THF$ (M = Gd and Yb). Thus, using proper stoichiometries and isolation procedures the following equation summarizes the cyclopentadienide syntheses:

$$MCl_3 + nNaC_5H_5 \xrightarrow{THF} (C_5H_5)_nMCl_{3-n} \cdot xTHF + nNaCl \qquad (I\text{-}1)$$

n = 3, x = 1, M = La-Lu, Y
n = 2, x = 1, M = Sm-Lu, Y
n = 1, x = 3, M = Sm-Lu

Though the principal interest here is with the 3+ oxidation state, it is to be noted that the dicyclopentadienides for the lanthanides with well known 2+ oxidation states (Sm, Eu, Yb) are accessible. For europium and ytterbium the preparation is as follows,[19]

$$M + 3C_5H_6 \xrightarrow{NH_3(\ell)} M(C_5H_5)_2\cdot xNH_3 + C_5H_8 \qquad \text{(I-2)}$$

$$M = Yb, Eu$$

$$M(C_5H_5)_2\cdot xNH_3 \xrightarrow[\text{1 hr}]{\substack{\text{vacuum}\\ 120\text{-}200°}} M(C_5H_5)_2$$

The cyclopentene in eq.(I-2) was identified by gas chromatography. That the reaction in eq.(I-2) may be subject to difficulties in obtaining purely divalent ytterbium was discussed in a note by Hayes and Thomas.[26] They isolated (by fractional sublimation) three compounds: $Yb(C_5H_5)_3$, $Yb(C_5H_5)_2$ and a dinuclear complex tentatively formulated as $(C_5H_5)_4Yb_2(NH_2)_2$.

Calderazzo *et al.*[24] provided the following synthetic route to ensure complete absence of any trivalent ytterbium in the product:

$$(C_5H_5)_2YbCl + Na \xrightarrow{THF} Yb(C_5H_5)_2\cdot xTHF + NaCl$$

$$Yb(C_5H_5)_2\cdot xTHF \xrightarrow[\text{4 hr}]{\substack{\text{vaccum}\\ \text{R.T.}}} Yb(C_5H_5)_2 \qquad \text{(I-3)}$$

The samarium compound is obtained by the following route,[25]

$$Sm(C_5H_5)_3 + KC_{10}H_8 \xrightarrow{THF} Sm(C_5H_5)_2{\cdot}THF + KC_5H_5 + C_{10}H_8 \quad (I\text{-}4)$$

In this case, according to the authors, the coordinated tetrahydrofuran could not be removed without decomposition. These compounds are extremely air sensitive and the bonding is believed to be largely electrostatic.

A common observation made in this field, which is also apparent in the previous equations, was that the cyclopentadienide complexes crystallized from donor solvents invariably contained coordinated solvent molecule(s). The Lewis base could only be removed by heat treatment under high vacuum. This prompted Fischer and Fischer to study the Lewis acidic behavior of the tricyclopentadienides.[27] The THF adducts, $M(C_5H_5)_3{\cdot}THF$ (M = Tb, Ho, and Yb), were readily isolated by crystallization from tetrahydrofuran. The complex $Yb(C_5H_5)_3{\cdot}NH_3$ was prepared by direct reaction of liquid ammonia with $Yb(C_5H_5)_3$. The ammonia adduct survived sublimation, indicating very strong bonding interaction between Yb and NH_3. The ammonia adducts of the lighter lanthanides however decompose upon sublimation.[15b] The reaction of triphenylphosphine with $Yb(C_5H_5)_3$ in benzene produced a crystalline product, $Yb(C_5H_5)_3{\cdot}PPh_3$, which could be obtained analytically pure by continuous extraction with pentane affording large black crystals. The final base used by these authors was cyclohexylisonitrile.

Again, direct reaction of the base and the tricyclopentadienide derivatives in benzene followed by sublimation at 150-160°C produced the corresponding $M(C_5H_5)_3 \cdot CNC_6H_{11}$ complexes (M = Nd, Tb, Ho, Yb, and Y). Adducts with cyclohexylisonitrile for the remainder of the lanthanide series were prepared by Kanellakopulos and von Ammon.[28] Based on infrared data the cyclohexylisonitrile is acting as a σ-donor (see discussion in Chapter III). This and the existence of vibrational bands in the 600-60 cm^{-1} region assigned to ring-metal modes, lead Fischer and Fischer[27] to conclude that there is some degree of covalence in the bonding of these complexes. Discussion of the utility of infrared data in obtaining information concerning the bonding in these and other π-carbocyclic organolanthanide complexes will be delayed until Chapter II.

As can be seen, the donors studied include both hard and soft bases as classified by Pearson.[29] This is not the typical behavior expected for tripositive lanthanide ions which normally prefer hard donors.[2,5,29] Although the synthesis requires anhydrous media employing non-donor solvents (unless the desired base is used as solvent) to avoid competition, the adducts so obtained are quite thermally stable albeit still very susceptible to oxidation and hydrolysis. The range of bases has been expanded to include pyridine,[30,31] (-)-nicotine,[31] N-methylpyrrolidine,[31] tri-n-butyl phosphine,[32] and diethyl sulfide.[32] The complex with diethyl sulfide was not actually isolated, adduct formation was ascertained only by ^{1}H NMR spectral study.

More exotic Lewis bases have been employed by Crease and Legzdins using the oxygen donor sites of metal-carbonyl and metal-nitrosyl complexes.[33] Infrared data were used as a measure of the acid-base interaction between tricyclopentadienide lanthanide complexes and $[(C_5H_5)Fe(CO)_2]_2$ $Co_2(CO)_8$, $[(C_5H_5)Ni(CO)]_2$, $(C_5H_5)Cr(NO)_2Cl$, and $(C_5H_4CH_3)Mn(CO)_3$; whereas shifts in the proton NMR spectra were cited as evidence for interaction with $(\eta^4-C_8H_8)Fe(CO)_3$ and $(C_5H_5)_2WH_2$, note that in the last complex the tungsten atom is the basic site.

It has been found recently that pyrazine (NC_4H_4N) produces the dimeric complex μ-pyrazine-bis[tris(cyclopentadienide)ytterbium(III)], upon sublimation of the crude reaction product.[34]

The foregoing paragraphs provide an overview of the cyclopentadienide complexes of the lanthanide elements and also give an indication of their strong Lewis acidic behavior. Further comments on the bonding in these complexes are referred to part 3 of the Introduction. It will be seen in the following section that the use of the cyclooctatetraenide dianion had a significant impact on the further development of organolanthanide chemistry.

ii) Cyclooctateraenide Complexes.

The synthesis of bis(cyclooctatetraenyl)uranium(IV), "uranocene," in 1968 by Streitwieser and Müller-Westerhoff[35] is credited with rekindling interest in the chemistry of organolanthanides and organoactinides.[36] It is significant to observe that in 1963 R. D. Fischer[37] had predicted the existence of cyclooctatetraenyl complexes of the actinides and postulated, especially for uranocene, covalent stabilization from the overlap of metal 5f orbitals with symmetry-allowed combination of the highest occupied M.O. of the cyclooctatetraenide ligand. Studies on uranocene and related compounds were conducted to test this postulate. Some of the investigations will be mentioned further on.

Uranocene itself was prepared by the straightforward reaction of anhydrous uranium tetrachloride and dipotassium cyclooctatetraenide:[35]

$$UCl_4 + 2K_2C_8H_8 \xrightarrow{THF} U(C_8H_8)_2 + 4KCl \qquad (I\text{-}5)$$

Surprisingly uranocene is stable in degassed water. This unexpected stability was somewhat reminiscent of the ferrocene story, and so it was hoped that the cyclooctatetraenide ligand would provide f-element metallocene derivatives similar to the corresponding cyclopentadienyls of the d-transition series. The vast number of studies that this lead to, for the actinide series, is beyond the scope of this introduction. Interested readers are referred to the Annual Surveys in the Journal of Organometallic Chemistry[12d] and to the reviews by Raymond *et al.*[10] and Marks.[38]

Shortly after the report by Streitwieser *et al.*,[35] Hayes and Thomas [39] reported the synthesis of the cyclooctatetraenide complexes of europium (II) and ytterbium (II). These were prepared by direct reaction of the metals with cyclooctatetraene in liquid ammonia and are exceedingly air sensitive compounds.

Streitwieser *et al.* continued their investigations with the dianion of cyclooctatraene by preparing two series of complexes with the tripositive lanthanides. The first was the bis(cyclooctatetraenide) complexes[40a,11] $K[M(C_8H_8)_2]$, which were prepared as follows:

$$MCl_3 + 2K_2C_8H_8 \xrightarrow{THF} K[M(C_8H_8)_2] + 4KCl \qquad (I\text{-}6)$$

M = Y, La, Ce, Pr, Nd, Sm, Gd, Tb.

Attempts to prepare the europium and ytterbium derivatives were unsuccessful. The second series was the monocyclooctatetraenide derivatives, $[(C_8H_8)MCl\cdot 2THF]_2$, which were prepared by the reaction of one equivalent of the anhydrous metal halide with one equivalent of the cyclooctatetraene dianion.[40b,11] The derivatives for M = Ce, Pr, Nd, and Sm were obtained. Mention is not made whether the synthesis of monocyclooctatetraenide derivatives of other lanthanide ions was attempted.

Both series of complexes are exceedingly air sensitive, and, unlike uranocene, they react violently with water. Discussion of the chemical and physical properties of these organolanthanides will be delayed until Chapters II and III but suffice it to say that Streitwieser *et al.*[11] concluded that the bonding between the lanthanide ion and cyclooctatetraenide ring is largely ionic.

Recently, Cesca *et al.* have synthesized some interesting cyclooctatetraene complexes. The following reactions summarize their preparations:[41,42]

$$\mathrm{Ce(O\text{-}i\text{-}C_3H_7)_4\cdot i\text{-}C_3H_7OH + 5Al(C_2H_5)_3 \xrightarrow[140°C]{C_8H_8,\ excess} Ce(C_8H_8)_2 + 5(C_2H_5)_2Al(O\text{-}i\text{-}C_3H_7) + C_2H_6 + 4C_2H_5} \qquad \text{(I-7)}$$

$$\mathrm{2Ce(O\text{-}i\text{-}C_3H_7)_4\cdot i\text{-}C_3H_7OH + 10(C_2H_5)_3Al + 3C_8H_8 \xrightarrow[Toluene]{100°} Ce_2(C_8H_8)_3 + 10(C_2H_5)_2Al(O\text{-}i\text{-}C_3H_7) + 2C_2H_6 + 8C_2H_5} \qquad \text{(I-8)}$$

$$\mathrm{Ce(O\text{-}i\text{-}C_3H_7)_4\cdot i\text{-}C_3H_7OH + 4(C_2H_5)_3Al \xrightarrow[100°C\ Toluene]{C_8H_8,\ excess} (C_8H_8)Ce(O\text{-}i\text{-}C_3H_7)_2Al(C_2H_5)_2\cdot 1/4C_7H_8 + C_2H_6 + 3C_2H_5} \qquad \text{(I-9)}$$

These are relatively novel compounds and as can be seen the products formed are quite sensitive to the stoichiometry of the reaction. Related to the cerium compound obtained in Eq (I-8) are complexes of the formula $[M(C_8H_8)(OC_4H_8)_2][M(C_8H_8)_2]$ where M = La, Ce, Nd, and Er.[14] These complexes were prepared by the reaction of metal atoms and cyclooctatetraene at -196°C followed by extraction with tetrahydrofuran. Some properties of these last complexes will be discussed in Chapter IV.

iii) Alkyls, Aryls, and Others.

A short discussion will now be given pertaining mainly to the alkyl and aryl compounds of the lanthanides to draw attention to σ-bonded derivatives of these elements. This area of organolanthanide chemistry is undergoing significant expansion.

In 1968 F. A. Hart *et al.*[43] reported the first σ-bonded derivatives of the lanthanides. By reacting phenyllithium with anhydrous metal halides two types of compounds apparently were formed, eqs. (I-10) and (I-11).

$$MCl_3 + 3LiC_6H_5 \xrightarrow[0°C]{THF/Ether} M(C_6H_5)_3 + 3LiCl \qquad (I-10)$$

M = Sc, Y

$$MCl_3 + 4LiC_6H_5 \xrightarrow[0°C]{THF/Ether} Li[M(C_6H_5)_4] + 3LiCl \qquad (I-11)$$

M = La, Pr

The compounds were thermally stable but insoluble pyrophoric solids and as a result their full characterization was lacking. These difficulties were overcome by the synthesis of tetrakis(2,6-dimethylphenyl)lutetiate (III).[44] This was the first well characterized σ-bonded lanthanide derivative and its X-ray structure unequivocally showed that the metal is surrounded by a tetrahedral array of ligands, making it the first known example of a four-coordinate lanthanide complex. The analogous ytterbium complex was also prepared, however attempts to extend the synthesis to the larger lanthanides proved unsuccessful. Nevertheless the importance of sterically demanding organic groups is readily apparent. Utilizing this concept several trimethylsilylmethyl substituted lanthanides have recently been synthesized,[45] eqs. (I-12), (I-13), (I-14).

$$MCl_3 + 3LiCH_2SiMe_3 \xrightarrow{THF} M(CH_2SiMe_3)_3(THF)_2 + 3LiCl \qquad (I\text{-}12)$$

M = Tb, Er, Yb

$$M(CH_2SiMe_3)_3(THF)_2 + LiCH_2SiMe_3 \xrightarrow{2L} [Li(L)_4][M(CH_2SiMe_3)_4] \qquad (I\text{-}13)$$

M = Y, Er, Yb; $L_2 = Me_2NCH_2CH_2NMe_2$

M = Y; L = THF

$$MCl_3 + 3LiCH(SiMe_3)_2 \xrightarrow{THF} [Li(L)_4][M\{CH(SiMe_3)_2\}_3Cl] + 2LiCl \qquad (I\text{-}14)$$

M = Er, Yb; L = THF

A different approach was to use the cyclopentadienide moiety to occupy coordination sites around the metal and thereby reduce the reactivity of the σ-bonded organolanthanide complex. Thus Tsutsui *et al.*[46] synthesized the compounds illustrated by eq. (I-15).

$$(C_5H_5)_2MCl + LiR \xrightarrow[-78°C]{THF/Ether} (C_5H_5)_2MR + LiCl \qquad (I\text{-}15)$$

M = Yb, Er, Gd; $R = C{\equiv}CC_6H_5$, C_6H_5, CH_3

M = Ho; $R = C{\equiv}CC_6H_5$

M = Sm, Er, Ho; $R = C_3H_5$

Once again the complexes were found to be thermally stable, thus demonstrating that the alkyl- and aryllanthanide bonds are not inherently weak.

Lappert *et al.* have extended the above reaction to include an alkylaluminate as the alkylating agent, but isolated interesting bimetallic derivatives instead of the presumably anticipated alkyllanthanide complexes,[47] eq.(I-16).

$$\tfrac{1}{2}[(C_5H_5)_2MCl]_2 + LiAlR_4 \xrightarrow{Toluene} [(C_5H_5)_2M(R_2AlR_2)] + LiCl \qquad (I\text{-}16)$$

M = Sc, Gd, Dy, Ho, Er, Tm, Yb; R = Me

M = Sc, Y; R = Et

The electron-deficient dialkyl-bridge in these compounds was established by ^1H and ^{13}C NMR data and by single crystal X-ray analysis of the yttrium and ytterbium complexes.[47,48]

Somewhat analogous electron-deficient bridged species were obtained by Marks and Grynkewich[49] in their synthesis of lanthanide tetrahydroborates, eq. (I-17). The bonding

$$(C_5H_5)_2MCl + \text{excess } NaBH_4 \xrightarrow{THF} (C_5H_5)_2MBH_4 \cdot THF + NaCl \qquad \text{(I-17)}$$

M = Sm, Er, Yb

mode of the tetrahydroborate moiety was assigned as tridentate in the samarium but only as bidentate in the ytterbium complex, showing once again the influence of the lanthanide contraction on coordination number in this area of chemistry.

Using the bimetallic complex of eq. (I-16), Lappert *et al.*[50] found an interesting new route to the $(C_5H_5)_2$-MCH_3 complexes previously synthesized by Tsutsui,[46] (eq. (I-18). However, as indicated in eq. (I-18), a

$$2[(C_5H_5)_2MMe_2AlMe_2] + 2py \xrightarrow{Toluene} [(C_5H_5)_2MMe]_2 + 2AlMe_3{:}Py \qquad \text{(I-18)}$$

M = Y, Dy, Ho, Er, Yb

single crystal X-ray study established methyl-bridged dimeric structures for the complexes instead of the monomeric formulation originally assigned by Tsutsui. Although the formation of associated species is understandable in this case in terms of the desire of the lanthanide ion to achieve a high coordination number, nevertheless the preponderance of electron-deficient bridge formation in these alkyl complexes is, at first sight, surprising. It indicates, perhaps, that the chemistry of these organolanthanides will find closer similarities to organoaluminum chemistry than anticipated.

Bimetallic complexes containing direct lanthanide-main-group element bonds have also recently been synthesized by Schumann,[51] eqs. (I-19) and (I-20). These molecules,

$$(C_5H_5)_2MCl + LiM'(C_6H_5)_3 \xrightarrow[-78°]{THF} (C_5H_5)_2M-M'(C_6H_5)_3 + LiCl \tag{I-19}$$

M = Er, Yb; M' = Sn

M = Er; M' = Ge

$$MCl_3 + 3LiM'(C_6H_5)_3 \xrightarrow{THF} M[M'(C_6H_5)_3]_3 + 3LiCl \tag{I-20}$$

M = Nd, Gd, Er; M' = Ge

M = Pr, Nd, Gd; M' = Sn

like most other organolanthanides, are thermally stable but extremely air sensitive materials.

The chemistry of the σ-bonded lanthanide derivatives just like the cyclopentadienide and cyclooctatetraenide complexes, centers almost exclusively on the 3+ oxidation state. A few attempts however have been reported concerning divalent lanthanide ions. D. F. Evans *et al.*[52] were first to synthesize such complexes. The direct reaction of lanthanide metals with alkyl and aryl iodides in tetrahydrofuran resulted in the formation of RMI (M = Eu, Yb) type species. Although characterized only in solution, the magnetic susceptibility data, analytic procedures, and typical Grignard-type reactions all supported the above formulation. Somewhat better characterized solid complexes of Yb^{2+} were synthesized by Deacon *et al.*,[53] eq. (I-21). The complexes are exceptionally

$$HgR_2 + Yb \xrightarrow{THF} R_2Yb \cdot nTHF + Hg\downarrow \qquad (I-21)$$

$R = C_6H_5;\ n = 4$

$R = C{\equiv}CC_6H_5;\ n = 0$

air sensitive and for the phenylacetylide derivative an associated structure is postulated.

Although not strictly in the realm of σ-bonded derivatives a recent report by W. J. Evans *et al.*[54] describes a very elegant approach for the synthesis of low oxidation state lanthanide complexes. These authors describe the cocondensation of lanthanide metals with not easily reducible organic ligands, specifically 1,3-butadiene and 2,3-dimethyl-buta-1,3-diene, eq. (I-22).

$$M(atom) + diene \xrightarrow[-196°]{} M(diene)_x$$

$M = Er, Nd, Sm, x = 3$ and diene $= C_4H_6$

$M = Er, La; x = 2$ and diene $= (CH_3)_2C_4H_4$

The compounds are oxidatively and hydrolytically unstable and the La derivative appears to be the first paramagnetic organolanthanum complex. Although the bonding and structures of these complexes is far from clear it appears, based on these results, that a wide variety of organic ligands not seriously considered in the past will be able to interact and form isolable and highly unusual organolanthanide complexes.

3. Comments on Bonding

It has already been indicated in reference to the cyclopentadienide lanthanide complexes that the metal to ring bonding is largely electrostatic.[15-17] Although, Fischer[27] has suggested a significant covalent component to the bonding in the tricyclopentadienides, this has not been substantiated by other studies nor accepted by other workers. Concerning the cyclooctatetraenide derivatives, the bonding also appears to be largely electrostatic, in contrast to the covalent bonding found in uranocene.[11]

In this section only a representative set of studies will be included to illustrate the manner in which f-orbital contribution to bonding has been considered.

First, let us look at uranocene and related compounds. In the first preparation of uranocene it was proposed that the interaction of 5f-orbitals with ligand π-orbitals is responsible for the charge-transfer spectra observed in the visible region, and for the stability of the molecule toward weak acids and degassed water.[35]

In support of this proposal Streitwieser and Harmon prepared uranocene with hydrocarbon substituents on the rings and noted shifts in the visibile spectra as a function of electron donating ability of the alkyl substituents.[55] Edelstein *et al.*[56] examined the magnetic data for uranocene, the analogous neptunium and plutonium complexes, and some alkyl substituted uranocenes on the basis of molecular orbital calculations which involved substantial mixing of ligand π- and metal f-orbitals. Similar conclusions were reached by Edelstein *et al.*[57] based on the ^{1}H NMR spectra of uranocene and its tetramethyl substituted analogue. The large upfield shifts in the spectra were shown to be the result of large positive net contact shift for which the most plausible mechanism was assigned to charge transfer from filled ligand π M.O.'s to vacant metal f-orbitals. Finally, there is data from the photoelectron spectrum of uranocene. Its interpretation by two groups suggests f-orbital involvement and also, previously not considered, involvement of 6d-orbitals.[58,59]

Similar approaches to the above have been used in looking at various organolanthanide complexes. The use of absorption spectra in determining the ability of the ligands to split the $4f^n$ multiplet terms has received varied interpretation. Fischer and Fischer[60] interpreted the large $4f^{12}$ multiplet splittings in the room temperature spectrum of $Tm(C_5H_5)_3$ as being the result of direct involvement between the 4f-orbitals and symmetry-allowed combination of ligand M.O.'s. However, Pappalardo[61] examined the spectra of the same compound down to liquid helium temperatures and concluded that the splittings found for $Tm(C_5H_5)_3$ were not exceptional but nevertheless were larger than usually observed in aquo systems. In addition Pappalardo *et al.* have also looked at the tricyclopentadienides of erbium[62] and ytterbium[63] (and base adducts) at liquid helium temperatures enabling them to reach the conclusion that the $4f^n$ electron configurations of the tripositive ions are relatively unperturbed and that the bonding is largely electrostatic. Nevertheless, there were some relatively large splittings that could involve weak covalency, and for the ytterbium complex an electron transfer band in the visible region was assigned as a ligand-to-metal charge transfer which would indicate at least some degree of overlap of ligand and metal orbitals.

Another feature of the absorption spectrum used to assess f-orbital participation in bonding is the position of the J levels relative to those in the aquo ion. The changes in band position (or nephelauxetic effect) can be related to covalency in the metal-ligand bonding as they reflect changes in interelectronic repulsion parameters.[64] Based on the small shifts Nugent *et al.*[65] concluded that the degree of covalency in the metal-ligand bonding of all tricyclopentadienide derivatives of the lanthanide metals is at most 5% more than in the corresponding aquo ions.

Other evidence suggesting a high degree of electrostatic character in the bonding comes from magnetic data. For the lanthanide tricyclopentadienides the effective magnetic moments were found to be very close to the free ion values and temperature independent.[15] Also the mono- and bis(cyclooctaterenide)lanthanide complexes were observed to have moments only slightly reduced from the free ion value.[11] No attempt was made to attach significance to these small differences. A molecular orbital approach was used twice by Warren[66,67] to interpret the limited magnetic data for $Ce(C_8H_8)_2^-$. In both calculations the 4f orbitals appear to have little involvement with the ligand π-orbitals, while in the second calculation there is some indication of utilization of 5d orbitals.

Thus, the spectral and magnetic data are in accord with the idea of well shielded 4f-orbitals unable to participate in metal-ring covalent interactions. However there is gathering evidence, based on molecular orbital calculations, that these complexes might possess small, but significant, covalent bonding components through ligand-5d orbital mixing.

The reactivity and physical properties of organolanthanide complexes as shown here also support the largely electrostatic bonding formulation in contrast to the actinide(IV) complexes discussed. As can be seen, the degree of covalent bonding in organolanthides is difficult to assess. The 4f-orbitals do not appear to be strongly involved in bonding, on the other hand, these orbitals contain the electrons whose properties are most readily observed and from which bonding conclusions are in turn drawn. Thus, the synthesis of new compounds will allow comparison of chemical and physical properties with existing compounds giving a greater basis from which to draw information; possibly produce complexes with new and interesting chemical and physical properties (volatility, reactivity, etc.); and provide a more complete understanding of organolanthanide chemistry.

CHAPTER TWO

SYNTHESIS AND PROPERTIES OF THE MIXED SANDWICH COMPLEXES $(C_5H_5)M(C_8H_8)$.

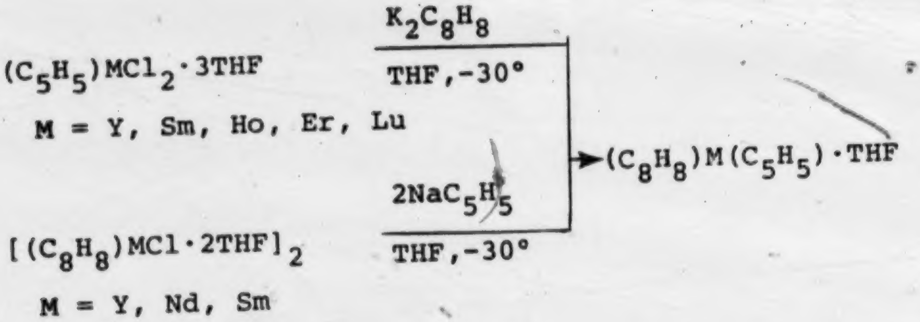
1. Introduction

From Chapter I it is clear that a wide variety of organolanthanide complexes can be obtained employing the cyclopentadienide and cyclooctatetraenide ligands. It is evident that the organometallic chemistry of the lanthanides can be further explored with the synthesis of neutral mixed sandwich complexes involving the two classes of ligands.

In this chapter the synthesis of (cyclopentadienide)-(cyclooctatetraenide)lanthanide(III) complexes for representative members of the lanthanide series and yttrium will be described. The properties of the complexes will also be compared to the analogous titanium and scandium derivatives, which are the only other compounds known to contain both the η^8-C_8H_8 and η^5-C_5H_5 ligands, and to the organolanthanides containing the individual ligands.

2. Synthesis

The two general routes employed for the synthesis of these mixed sandwich complexes are given by equation (II-1).



$$(C_5H_5)MCl_2\cdot 3THF \xrightarrow[\text{THF},-30^\circ]{K_2C_8H_8} (C_8H_8)M(C_5H_5)\cdot THF \qquad \text{(II-1a)}$$

M = Y, Sm, Ho, Er, Lu

$$[(C_8H_8)MCl\cdot 2THF]_2 \xrightarrow[\text{THF},-30^\circ]{2NaC_5H_5} (C_8H_8)M(C_5H_5)\cdot THF \qquad \text{(II-1b)}$$

M = Y, Nd, Sm

$$(C_8H_8)M(C_5H_5)\cdot THF \xrightarrow[50^\circ,\text{1-2 hr}]{\text{vacuum}} (C_8H_8)M(C_5H_5) \qquad \text{(II-2)}$$

It was necessary to utilize the reactions shown in both eq. (II-1a) and eq. (II-1b) as a result of the availability of the starting materials. In Chapter I it was noted that Dubeck *et al.*[17] were unable to synthesize $(C_5H_5)MCl_2$ complexes, Eq (II-1a), for the larger lanthanide elements which precede samarium. Their report did not include yttrium, but the similarity of the ionic radius of trivalent yttrium compared to trivalent holmium (see Table I), and the general similarities of lanthanide chemistry compared to that of yttrium suggested the preparation of $(C_5H_5)YCl_2$; the preparation proved to be successful. Similarly, Streitwieser *et al.*[11] did not indicate whether their synthesis of $(C_8H_8)MCl$ complexes could be extended to the later lanthanides. The preparation of the yttrium mixed sandwich complex was undertaken *via* Eq (II-1b) by the *in situ* reaction of $(C_8H_8)YCl$ with NaC_5H_5. The success of this route indicates that similar $(C_8H_8)MCl$ complexes could be obtained for other heavy lanthanides. Complete experimental details will be found in the final Chapter of this thesis, only an outline of the synthetic method will be given below.

All the mixed sandwich compounds prepared in this study are pyrophoric and exceedingly water sensitive. This necessitated rigorous exclusion of air and water from solvents and the reactants employed. It was also necessary to work under an atmosphere of scrupulously purified nitrogen employing standard Schlenk techniques.[71] A double manifold (vacuum/nitrogen) was also standard in order to facilitate manipulations. Modification of any procedures to enable handling these very air sensitive compounds will also be discussed in the final Chapter.

For preparation according to eq. (II-1a), a solution of dipotassium cyclooctatetraenide was added dropwise to a tetrahydrofuran solution of the appropriate dichloro-(cyclopentadienide)lanthanide(III) complex at about -30°C. The temperature was maintained near -30°C for 1-2 hrs after addition was complete and then allowed to slowly warm to room temperature. After a total reaction time of 15-18 hours the precipitated potassium chloride was removed by filtration. The clear filtrate was then concentrated *in vacuo* to the point of crystallization and hexane was added. Cooling at -20°C for up to 36 hours, produced well formed crystals which were isolated by filtration and identified as the tetrahydrofuran adduct of the neutral mixed sandwich complex. This indication of Lewis acid behavior provides the subject matter for Chapter III. The tetrahydrofuran is readily removed by vacuum drying at 10^{-3} mmHg and 50°C leaving the unsolvated, neutral mixed sandwich complex. Employing essentially similar experimental procedures but starting with $(C_8H_8)MCl$, Eq (II-1b), mixed sandwich complexes of the early lanthanide elements also became accessible.

Although the reactions represent simple metathetical displacement of the chloride by the anionic carbocyclic ligands, the preparations are plagued with undesired side reactions or possibly disproportionation of the $(C_8H_8)M(C_5H_5)\cdot THF$ complexes (for instance $M(C_5H_5)_3$ was sometimes obtained). A thorough discussion of the problems associated with the preparation will be given in Chapter IV. Suffice it to say here that the isolated yield of pure, unsolvated complexes is poor (of course the removal of the coordinated THF molecule is quantitative). The yields are in the 35-48% range for Y, Ho, Er, and Lu, while for samarium, a particularly troublesome metal, only after several crystallizations could the pure $(C_8H_8)Sm(C_5H_5)$ be obtained and then only in about 6% yield. Furthermore it was also noticed that the isolation procedure was more difficult and final yields even lower when the preparative method of Eq (II-1b) was employed. This method thus was abandoned as a preparative route to the mixed sandwich complexes of the heavier lanthanides.

The formulation of these organolanthanide complexes as indicated in Eq (II-2) is supported by a combination of spectroscopic methods, mass spectrometry, and elemental analysis.

3. Results and Discussion

i) Physical Properties

It appears from the representative compounds synthesized that the (cyclooctatetraenide)(cyclopentadienide)lanthanide(III) complexes could be prepared for any member of the lanthanide series as well as for yttrium. As already mentioned, all the complexes are very air and moisture sensitive, and Lewis acidic behavior is suggested by virtue of isolation of tetrahydrofuran adducts. The THF, however, can be readily removed by vacuum drying. Qualitatively it appears that the removal of coordinated THF is more facile than in the case of the $M(C_5H_5)_3 \cdot THF$ complexes. All the compounds are thermally stable up to 120°C *in vacuo*. Furthermore the yttrium and lutetium complexes can be sublimed readily, the former at 100°C and 10^{-3} mmHg and the latter at 115°C and 10^{-4} mmHg. These are not the minimum conditions for sublimation since slow sublimation at 80°C and 10^{-4} mmHg has been found to yield well defined crystalline products for both complexes. Prolonged heating, however, does result in significant decomposition. None of the other complexes could be sublimed, though rapid sublimation up to 215°C were attempted. This behavior is in contrast to the tricyclopentadienides of Birmingham and Wilkinson[15] which were sublimable typically at 200-230°C and 10^{-4} mmHg. Whether the considerable ease of sublimation of the yttrium and lutetium mixed sandwich compounds is reflected in solid state structural differences compared to the $M(C_5H_5)_3$ and the other $(C_8H_8)M(C_5H_5)$ complexes will have to await X-ray structural determination. On the other hand, thermal stability and even volatility cannot be taken as sole evidence for significant covalent metal-ring interaction. As noted the $M(C_5H_5)_3$ complexes do sublime but have been shown to be largely ionic. In addition, Streitwieser[11] has shown that $K_2C_8H_8$, a most assuredly ionic compound, can also be sublimed. Finally, the mixed sandwich complexes are moderately soluble in basic solvents such as pyridine and tetrahydrofuran from which the base adduct can be crystallized, exhibit low solubility in toluene and benzene, and are insoluble in hexane. The complexes are decomposed by methylene chloride and carbon disulfide.

ii) Infrared Spectra

Infrared spectroscopy has proved to be a valuable tool in examining the mixed sandwich complexes. The data, as will be shown, can be used to obtain information concerning the mode and type of bonding that exists between the two carbocyclic rings and the central lanthanide ion.

In Figure 1 the spectra in the 600-1600 cm^{-1} region for an early (neodymium) and late (holmium) lanthanide complex along with that for $(C_8H_8)Y(C_5H_5)$ are given. Table 3 lists the infrared absorptions in the same region for all the compounds studied. Inspection of Figure 1 and Table 3 shows a good correspondence in position and relative intensity of the absorption bands for the members of the lanthanide series and yttrium indicating that the overall molecular structure of all the complexes are closely related. The significance of the number, position, and intensity of the bands will now be discussed.

A substantial amount of data has been collected by Fritz relating the number of bands and band positions in the infrared spectra of metal complexes of carbocyclic rings to the mode of bonding between the C_nH_n ring and the metal.[73] The approach suggested by Fritz has been utilized by a number of investigators[19,69,72,74,75] and has also been recently reviewed by Maslowsky[76] who also

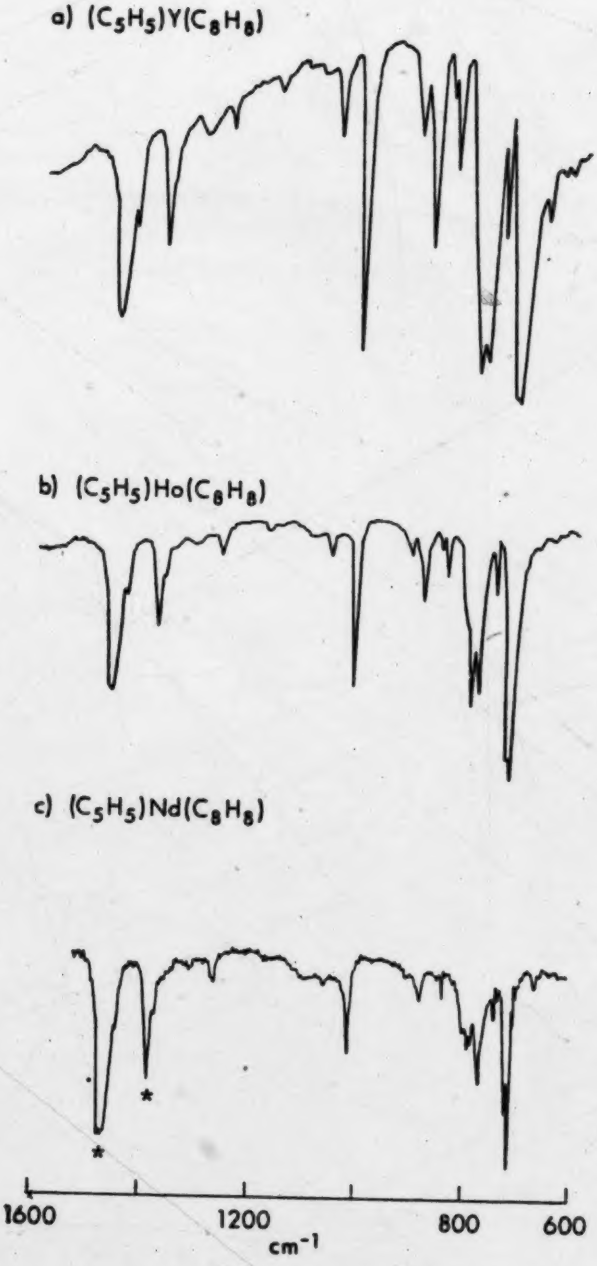


Figure 1: Infrared spectra of $(C_5H_5)M(C_8H_8)$ Complexes; M = Y, Ho, Nd. Recorded as mineral oil mulls. *mineral oil.

Table 3. Infrared Spectra of $(C_5H_5)M(C_8H_8)$ Complexes[a,b]

Ti[c]	Sc[d]	Nd	Sm	Y	Ho	Er	Lu	Assignment[e]
1441m	1430m-s	1437m	1435w-m	1432m	1434m	1431m	1433w-m	$C_5H_5, \nu_a(C-C) + C_8H_8, \nu_a(C-C)$
1427s								
1369m								
1323m	1325m	1305w	1305vw	1305w	1306w	1306vw	1308vw	
1265w		1261w	1261w	1261w	1259w	1259w		
1108m	1113w							$C_5H_5, \nu_s(C-C)$
1066w		1059w		1059w-m	1059w			
1012s	1018s	1011s	1012s	1013s	1015s	1016s	1015s	$C_5H_5, \delta(C-H)$
1003s	1002s							
				910w-m	909w			
911s	900s	882m-s	879w-m	883m-s	886m-s	895m	895w-m	$C_8H_8, \delta(C-H)$
855vw				850w	850w			
		839m		841m	841w-m			
815w		801m	801w		803w,sh			

continued......

Table 3. (continued)

797vs	800s	789m-s	789s,sh	792s	798s	792s	795s	C_5H_5, γ(C-H)
793w,sh	790s	772s	772s	779s	780s	783s	787s	
	750m-s	747m	750w	750m	750m	750w		
761vs	729s	727s	727s	727s	730s	719s	720s	C_8H_8, γ(C-H)
748vs	714s	717s	719s	719vs	722vs	712s	712s	

[a] Spectra recorded as mineral oil mulls; frequencies in cm^{-1}.

[b] Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

[c] Values taken from Ref. 72.

[d] Values taken from Ref. 69.

[e] See Text for discussion and definition.

considered the relevance of new data.

Let us first consider this approach in relation to the C_5H_5 ligand. The cyclopentadienyl ligand can bond to a metal in a monohapto(η^1-C_5H_5) or pentahapto(η^5-C_5H_5) fashion. In η^5-C_5H_5 complexes we can further distinguish ionic and covalent bonding between the cyclopentadienyl moiety and the metal. In purely ionic compounds one can reasonably approximate the ligand as free $C_5H_5^-$ possessing D_{5h} symmetry. However, when complexed to a metal with strong covalent interactions, as (η^5-C_5H_5)M, the whole C_5H_5M fragment must be considered and the symmetry is reduced to C_{5v}. It is of course logical to assume that for a real molecule the spectral features expected for the covalent MC_5H_5 model will be displayed more strongly as the covalent nature of the metal-C_5H_5 bond increases. In complexes where the actual symmetry may differ from C_{5v}, the local symmetry of the (η^5-C_5H_5)M moiety (i.e., C_{5v}) is applied to the discussion of the infrared spectra.[73,76]

For D_{5h} symmetry there are four normal modes of vibration which are infrared active for the cyclopentadienide anion. These are the asymmetric C-H stretch, ν_a(C-H), the asymmetric C-C stretch (or ring breathing mode), ν_a(C-C), the in-plane C-H bending, δ(C-H); and the out-of-plane C-H bending, γ(C-H). Vibrational data for typical ionic cyclopentadienide complexes are collected in Table 4.

Table 4. Infrared Active Modes for Some Ionic Cyclopentadienide Complexes[a,b]

Normal Mode	KC_5H_5	RbC_5H_5	$Sr(C_5H_5)_2$	$Ba(C_5H_5)_2$
ν_a(C-H)	3048	3030	3077	3065
ν_a(C-C)	1455	1501	1435	1435
δ(C-H)	1009	1011	1008	1009
γ(C-H)	702	696	739	736

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[a] Frequencies in cm^{-1}.

[b] Data from Ref. 76.

As the strength of the metal-ring interaction increases the metal and the C_5H_5 ligand must be considered together as the $(\eta^5\text{-}C_5H_5)M$ fragment. The symmetry is C_{5v} and the C_5H_5 moiety will give rise to seven active normal modes in the infrared. These are, in addition to the four modes already mentioned for the ionic cyclopentadienides, an additional out-of-plane C-H bending, γ(C-H), a symmetric C-H stretch, ν_sCH, and a band near 1100 assigned as a symmetric C-C stetch, ν_s(C-C), by Maslowsky[76] or as an out-of-plane bending vibration, γ(C-H), by Fritz.[73] Thus based on the number of strong vibrations observed in a metal-cyclopentadienyl complex, Fritz described the metal-ring bonding as ionic or covalent. In the C_{5v} covalent compounds he has also made further distinction between "centrally-σ-bonded" complexes and "genuine π-complexes". Tables 5 and 6 give some examples of the complexes that Fritz assigns to the above two classes. It seems that a more appropriate way to look at the infrared data in Tables 4-6 is to assign $Rb(C_5H_5)$ as representing the extreme of ionic bonding and to take $Ru(C_5H_5)_2$ as the extreme for covalent bonding with the remaining complexes comprising a gradual, more or less continuous variation in bonding between the extremes. It is apparent from the Tables that although the majority of the vibrational modes vary in a relatively narrow range, three of the bands change in a systematic way with

Table 5. Infrared Active Modes for Some "Centrally σ-Bonded" Cyclopentadienide Complexes[a,b]

Normal Mode	LiC_5H_5[a]	NaC_5H_5[b]	$Mg(C_5H_5)_2$[b]	$Ca(C_5H_5)_2$[c]
ν_a(C-H)	3048	3048	3067	3078
ν_s(C-H)	2906	2907	2913	2963
ν_a(C-C)	1426	1422	1428	1433
ν_s(C-C)	1120	1144	1108	1122
δ(C-H)	1003	998	1004	1009
γ(C-H)	-	-	779	780
γ(C-H)	746	712	758	751

[a] Frequencies in cm^{-1}.

[b] Data from Ref. 73.

[c] Data from Ref. 77.

Table 6. Infrared Active Modes for Some π-Bonded Cyclopentadienyl Complexes[a,b,c]

Normal Mode	$(C_5H_5)TiCl_3$	(C_5H_5)-$V(C_7H_7)$	$Fe(C_5H_5)_2$	$Ru(C_5H_5)_2$
ν_a(C-H)	3058	3039	3086	3097
ν_s(C-H)		2941	2909	
ν_a(C-C)	1435	1421	1408	1410
ν_s(C-C)	1124	1108	1104	1101
δ (C-H)	1017	1012	1001	1002
γ (C-H)	816	818	854	866
γ (C-H)	797	803	814	821

[a] Assignments made for C_{5v} local symmetry.

[b] Frequencies in cm^{-1}.

[c] Data from Ref. 73.

the nature of the metal-ring bond. As the ionic character of this bond increases the γ(C-H) frequency falls and is found below 800 cm^{-1}, at the same time the ν_a(C-C) vibration appears to increase in frequency although the change is not as regular as the variation in γ(C-H). The other important feature is the band near 1100 cm^{-1}, absent by symmetry for the D_{5h} ionic extreme, very weak in largely ionic compounds it is a strong feature in complexes such as ferrocene. The diagnostic value of these frequencies is clearly indicated. However, the form of the correlation between percent ionic character and band position and intensity is not known. Only qualitative arguments can be drawn concerning the bonding based on infrared data.

It is to be noted that the data given in Tables 4-6 are for the main bands in the spectra. There are additional weaker bands which can arise from solid state effects and also from coupling of vibrations in the complexes with more than one ring. Nevertheless, the observation of a simple infrared spectrum featuring only a few strong bands can be taken to indicate symmetrical bonding expected for an η^5-C_5H_5 ring. Contrary to this an (η^1-C_5H_5)M system, which can at best have C_s symmetry, is known to have a very rich and complex spectrum, there are twenty-four allowed normal modes of vibration from the C_5H_5 group itself. The distinction between η^5- and

η^1-C_5H_5 is a relatively easy task indeed. Caution should be exercised however when solid state structural inferences are made from infrared data. A case in point is the tricyclopentadienide derivatives of lanthanides. Table 7 lists the complete spectra. Although somewhat complicated, the simple ν(C-H) region, the absence of a relatively strong ν(C=C) band and the appearance of strong absorptions in regions previously ascribed to pentahaptocyclopentadienyl ring vibrations can be taken as evidence for predominantly symmetric metal-ring interaction. The largely electrostatic character of this bond is suggested by the low frequency of the γ(C-H) vibrations and the weak ν_s(C-C) band at 1120 cm^{-1}, a conclusion which is in accord with the magnetic and electronic spectral data and the reactivity of the complexes discussed in Chapter I. However to suggest that the data is consistent with a solid state structure comprising isolated $M(\eta^5$-$C_5H_5)_3$ molecules of D_{3h} symmetry would be foolhardy at best. Indeed the structure of tris(methylcyclopentadienide)neodymium(III) has been determined.[78] Each Nd^{+3} ion is surrounded by three η^5-C_5H_4Me rings and an η^1-C_5H_4Me moiety which is simultaneously η^5-bonded to another neodymium ion thus bridging two lanthanide ions together and creating a polymeric solid state arrangement. That the η^1-ring-metal bonding is due primarily to ionic rather than covalent bonding is suggested by the equivalence

Table 7. Infrared Spectra of $M(C_5H_5)_3$ Complexes[a,b,c]

M = Tb	Ho	Tm	Lu	Assignment
3077w	3077w	3072w	3072w	ν(C-H)
2941w	2941w	2915w	2937w	
1658w	1656w	1656w	1669w	
1443m	1443m			
1435m	1435m	1439m	1438m	ν_a(C-C)
1351w	1351w	1353w	1357w	
1120w	1120w	1119w	1119w	
1063m	1066m	1065m	1072m	
			1057m	
1006s	1005s	1009s	1007s	δ(C-H)
887m	887m	890m	890m	
842m	841m	845m	855s	
798s,br	792s,br	794s,br	800s,br	
770vs,br	771vs,br	774vs,br	776vs,br	γ(C-H)
622m	621m	625m	620m	

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[a] Values from Ref. 19

[b] Frequencies in cm^{-1}; abbreviations, see Table 3; br = broad.

[c] Spectra recorded as mineral oil mulls.

of the carbon-carbon bond lengths of the the cyclopentadienide rings. Thus, as the authors point out, there appears to be no significant changes in the delocalized electron system of the cyclopentadienide rings which might be manifested in bond length changes. Hence, the application of local C_{5v} symmetry to the major infrared bands is retained. The η^1-coordination is ascribed to the desire for neodymium to complete its coordination sphere.

A similar symmetry analysis can be applied to the C_8H_8 ring though a much more limited data set is available. Hocks *et al.*[74] examined the vibrational spectra for the bis(cyclooctatetraenyl) compounds of uranium and thorium. Though uranium and thorium have been shown to possess the D_{8h} structure in the solid state the spectra are again more complex in the 600-1600 cm^{-1} region than for the D_{8h} cyclooctatetraene dianion as approximated by the dipotassium salt (see Table 8). The out-of-plane C-H deformation again seems sensitive to the metal-ring bonding character. It was well established for uranocene that a substantial degree of covalent character exists in the bonding.

In the light of the data in Tables 4-8, the data for the mixed sandwich complexes of Table 3 can be re-examined. The assignments listed in the Table appear to be most reasonable based on the positions and

Table 8. Infrared Spectra for C_8H_8 Complexes[a]

$K_2C_8H_8$[b]	$U(C_8H_8)_2$[c]	$K[Ce(C_8H_8)_2]$[d]	$K[Y(C_8H_8)_2]$[d]	Assignment
1431m				ν_a(C-C)
	1320m	1280w		
		1070w	1048s	
		1000w		
880s	900s	875m	892s	δ(C-H)
	845w		880s	
	792m	790w		
		730w	740s	
		720w	706m,sh	
684s	777m	670s	684s	γ(C-H)
	746s		662s	

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[a] Frequencies in cm^{-1}; abbreviations as in Table 3.

[b] Data from Ref. 73.

[c] Data from Ref. 74.

[d] Data from Ref. 11.

intensities of the corresponding bands of the model compounds appearing in Tables 4-8. They receive further support from the analogous $(C_8H_8)M(C_5H_5)$ (M = Sc and Ti) complexes where essentially identical assignments for the major absorptions were made.[69,72] The structure of the titanium complex is known to consist of two parallel symmetrically bound carbocyclic ligands.[79] As expected from this structure, the infrared spectrum is simple, being essentially a superimposition of the bands expected from $(\eta^5-C_5H_5)M$ (C_{5v} symmetry) and $(\eta^8-C_8H_8)M$ (C_{8v} symmetry) molecular fragments. The symmetry of the whole molecule is of course less than the local symmetry of the individual fragments which might explain the appearance of some additional, mainly weak, bands. Nevertheless, it is apparent that the local symmetry approximation is largely valid in this case. A comparison of the infrared spectra for the titanium mixed sandwich complex with those of the analogous lanthanide and yttrium compounds quickly reveals substantial similarity in the number of observed bands, implying that the lanthanide mixed sandwich complexes also possess two symmetrically bound carbocyclic ligands. Whether the appearance of extra bands in the spectra of lanthanide complexes is due only to the slight breakdown of the local symmetry approximation, as mentioned for $(C_8H_8)Ti(C_5H_5)$, or it is diagnostic of more severe solid state structural changes similar to the associated structure found in $Nd(C_5H_4CH_3)_3$[78] must await the results of X-ray structural work on representative complexes.

The major differences seen in the infrared spectra when comparing the titanium complex to the lanthanide mixed sandwich derivatives can be traced to the bands that were shown before to be diagnostic of the metal-ring bonding, ionic or covalent. The absence of a ν_s(C-C) band around 1100 cm^{-1}, the low frequency observed for the out-of-plane C-H bending mode in the lanthanide and yttrium complexes are both suggestive of a substantial electrostatic component in the ligand to metal interactions. However the bonding may not be totally devoid of covalent character. As can be seen in Table 3, the out-of-plane C-H bending mode of both C_5H_5 and C_8H_8 ligands are split into two strong components indicating perhaps a relaxation of the D_{5h} and D_{8h} selection rules that would govern free ionic $C_5H_5^-$ and $C_8H_8^{2-}$ moieties, thereby suggesting some covalency.* The frequency of this mode for the C_8H_8 ring is, as expected, higher than in the anionic $M(C_8H_8)_2^-$ lanthanide complexes, Table 8. The crystal structure of the cerium compound[80] shows it to consist of two planar, symmetrically bonded eight-membered rings. Although the properties of this and related compounds were taken by Streitwieser to indicate largely ionic bonding, Clack and Warren[67] have argued based on M.O. calculations, that there is some ligand-to-metal d orbital mixing in the metal-ring interactions. Accepting the validity of the calculations, based on the infrared results it is likely that orbital overlap between the metal and the C_8H_8 ring is also occurring in the mixed sandwich complexes. Another interesting piece of information that has relevance to the bonding, comes from the variation in frequency of these out-of-plane bending modes on going from Ti to Sc to the lanthanide mixed sandwich complexes. It is apparent from Table 3 that for the C_5H_5 group vibration there is no change from Ti to Sc and then only a relatively small drop in frequencies for the lanthanide derivatives (although one of the components of the band experiences a larger decrease at least for the lighter lanthanides), whereas for the C_8H_8 moiety there is a more substantial drop between Ti and Sc but thereafter the band position remains remarkably constant. A speculative rationale for this trend can be obtained by looking at the bonding and electronic structure of $(C_5H_5)Ti(C_8H_8)$[81,82,83] and

---

*We cannot strictly rule out solid state effects as being responsible for this splitting, the fact that they are observed in both Ti and Sc complexes seems to mitigate against this. Nevertheless, it should be noted that splitting of the γ(C-H) band was observed in $M(C_5H_5)_3$ complexes of the lanthanides, Table 7, which are known to have polymeric structures. Solid state association of the mixed sandwich complexes also would be expected based on their Lewis acidic character. The need for structural work on these complexes is clear.

$(C_5H_5)Sc(C_8H_8)$.[84] Figure 2a shows the M.O. diagram for the titanium complex according to de Liefde Meijer,[84] while Figure 2b shows the most probable metal-ligand interactions. Also shown in the Figure is the symmetry allowed metal f orbital-C_8H_8 interaction. Based on photoelectron spectral data Green[82] has concluded that the M.O.'s of δ symmetry are of major importance for the bonding between early transition metals and C_8H_8 rings (overlap of metal $d_{x^2-y^2}$, d_{xy} and ring e_2 orbitals) whereas for the bonding between five-membered rings and the metal the most important contribution comes from M.O.'s of π-symmetry (e_1 orbitals of the C_5H_5 ring and metal d_{xz}, d_{yz} orbitals). They have also concluded that these π orbitals are mainly ligand in character. This of course is apparent in the M.O. scheme of Figure 2a which shows the C_8H_8 e_2 orbitals closer in energy to the metal orbitals than the e_1 orbitals of the C_5H_5 ring. Thus a change in metal orbital energy will have a greater effect on the charge of the C_8H_8 ring than on the charge of the C_5H_5 ring. This has been verified by de Liefde Meijer *et al.* from ESCA measurements on the Ti[81] and Sc[84] complexes. They find that whereas the charge on the C_5H_5 ring remains the same, the charge on the C_8H_8 moiety has increased on going from Ti to Sc. This is exactly the effect that would have been predicted from the infrared data, i.e., apparently no bonding change between the metal and C_5H_5 ring but

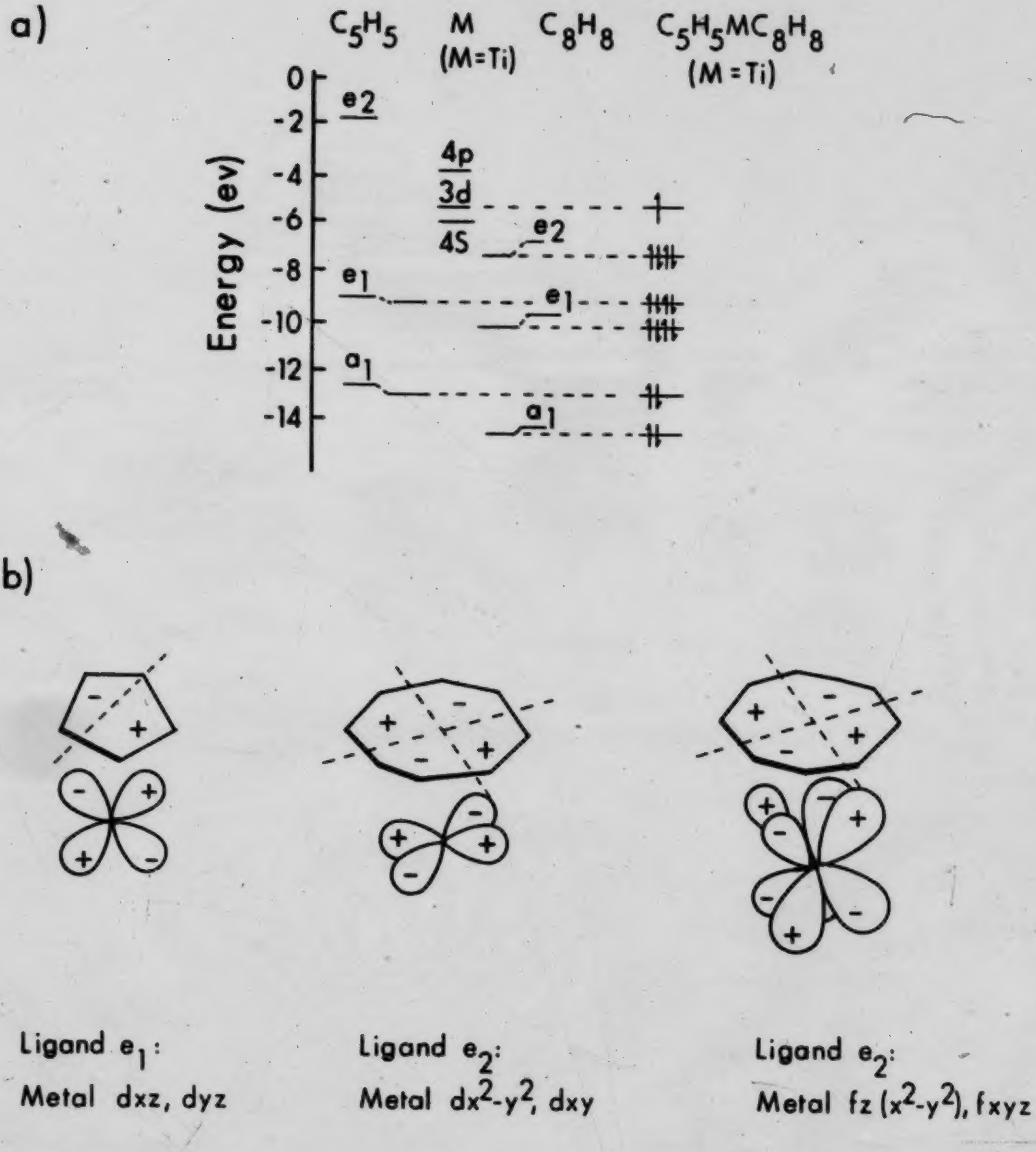

a)
C_5H_5
M
(M=Ti)
C_8H_8
$C_5H_5MC_8H_8$
(M=Ti)
Energy (ev)
0
-2
-4
-6
-8
-10
-12
-14
e2
4p
3d
4S
e2
e1
e1
a1
a1
b)
Ligand e_1:
Metal dxz, dyz
Ligand e_2:
Metal dx^2-y^2, dxy
Ligand e_2:
Metal $fz(x^2-y^2)$, fxyz

Figure 2. a) Qualitative M.O. Diagram for a Transition Metal $(C_5H_5)M(C_8H_8)$ Complex.

b) Symmetry Allowed interactions between Metal d- and f-Orbitals and Highest Filled Ligand Orbitals.

increased ionicity of the metal-C_8H_8 bonding. Whether this correlation can be extended to the lanthanide mixed sandwich complexes is not known. Indeed the slight decrease in the γ(C-H) vibration of the C_5H_5 ring on going from Sc to the lanthanides and the rise of one of the components of this frequency on proceeding from Nd to Lu while the C_8H_8 ring frequency remains constant already point out some difficulties with the simple model. Furthermore it is not our intention to imply that the bonding in the lanthanide mixed sandwich complexes is even as covalent as in the scandium compound. However it will be shown that further spectral properties of these complexes seem to be in accord with the greater involvement of the C_8H_8 ring orbitals with the lanthanide ions as compared to the interaction with the C_5H_5 ring orbitals. Of course greater involvement need not mean less polar M-C_8H_8 bonding. Indeed, as will be observed, the reactivity of these complexes points, not unexpectedly, to greater charge density on the C_8H_8 ring than on the C_5H_5 moiety.

In conclusion the infrared data indicate that $(C_5H_5)M(C_8H_8)$ complexes are sandwich type molecules comprised of symmetrically bonded planar five- and eight-membered rings. The bonding between the lanthanide ion and the rings is largely ionic. Although the evidence is indirect the bonding seems nevertheless to possess some covalent contribution most probably through metal d and ligand orbital mixing.

iii) Mass Spectra

As previously mentioned the yttrium and lutetium complexes are readily sublimable, the other compounds are volatile and stable enough to exhibit parent ions in their mass spectra. The observation of the parent ions for all the mixed sandwich complexes provided unequivocal evidence for their formation, and functioned as an indirect measure of purity with respect to volatile by-products especially in regard to $M(C_5H_5)_3$ complexes which, as mentioned, sometimes contaminated the original crude products.

Table 9 lists the fragments for the most abundant metal containing ions and Figure 3 gives a partial fragmentation scheme for the holmium complex supported by observation of appropriate metastable peaks. A complete listing of fragment ions will be given in the final Chapter for some of the complexes.

The data in Table 9 suggest some differences in the decomposition pathways for the mixed sandwich complexes within the mass spectrometer. It is immediately apparent that the relative abundance of the parent ion for the neodymium and samarium complexes is substantially lower than for the other members of the Table indicating lower stability of the $C_{13}H_{13}M^+$ ion for the early lanthanides.

Table 9. Relative Abundance for Major Metal Containing Fragments in the Mass Spectra of $(C_5H_5)M(C_8H_8)$ Complexes[c]

M	$C_{13}H_{13}M^+$	$C_{11}H_{11}M^+$	$C_8H_8M^+$	$C_5H_5M^+$	C_2HM^+	M^+	°C Source Temp.
Nd	47	<.4	81	100	11	20	170°
Sm	25	-	2.0	100	5	21	150°
Y	100	8.2	44	33	8.6	8.6	85°
Ho	100	4.0	46	57	10	26	130°
Er	100	5.4	41	51	9.1	25	115°
Lu	100	10	10	71	7.7	18	105°
Sc[a]	100	17	28	95	18	20	-
Ti[b]	100	17	<10	74	14	14	-

[a] Data from Ref. 69; source temperature not given.

[b] Data from Ref. 68; source temperature not given.

[c] Ionizing voltage = 70 eV.

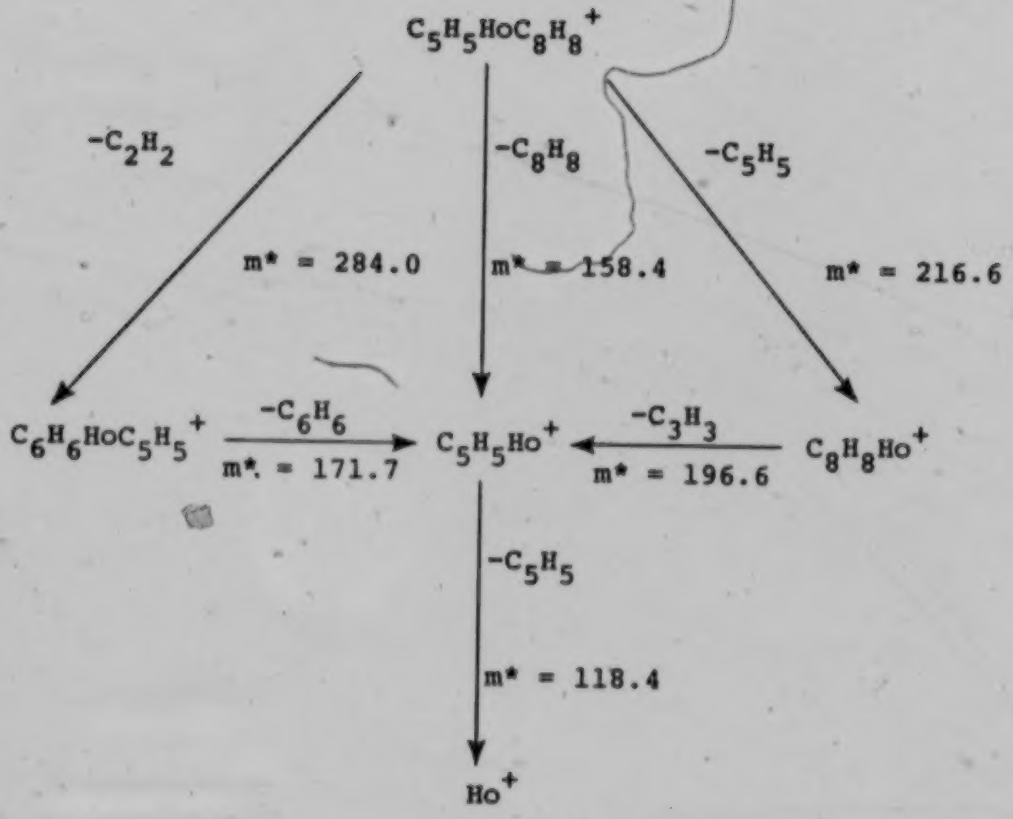

$C_5H_5HoC_8H_8^+$
$-C_2H_2$
$m^* = 284.0$
$-C_8H_8$
$m^* = 158.4$
$-C_5H_5$
$m^* = 216.6$
$C_6H_6HoC_5H_5^+$
$-C_6H_6$
$m^* = 171.7$
$C_5H_5Ho^+$
$-C_3H_3$
$m^* = 196.6$
$C_8H_8Ho^+$
$-C_5H_5$
$m^* = 118.4$
Ho^+

__Figure 3__. Partial Fragmentation Scheme of $(C_5H_5)Ho(C_8H_8)$.

Also, for M = Nd, Y, Ho, and Er there is no significant difference in the abundance of the $C_5H_5M^+$ and $C_8H_8M^+$ fragments within each spectrum in contrast to M = Lu, Sc, and Ti where $C_5H_5M^+$ is relatively more abundant. This difference is in keeping with the larger sizes of Y and the lanthanides which would be expected to favor bonding to the larger ring. The $C_5H_5M^+$ ion is also much more abundant in the samarium complex compared to $C_8H_8M^+$. However, this may reflect the well known stability of the 2+ oxidation state for the element, thus, decomposition *via* the neutral C_8H_8M moiety would be favorable, and in the $C_5H_5M^+$ fragment the samarium is formally in the 2+ oxidation state. The same behavior will be seen in Chapter III for the base adducts of the ytterbium complex which also has a relatively stable 2+ oxidation state.

The differences noted above seem to point to a slight gradation in properties as one proceeds from neodymium to lutetium such that the decomposition pathway for the relatively small lutetium 3+ complex more nearly resembles that for the titanium and scandium complexes. The infrared data might also be taken to suggest a similar variation when looking at the out-of-plane bending vibration for the cyclopentadienide moiety, Table 3. The frequency is lower for the lighter lanthanides (Nd, Sm), and approaches the position of $(C_5H_5)Sc(C_8H_8)$ in the lutetium mixed sandwich complex.

The partial fragmentation scheme shown in Figure 3 also shows differences in proceeding from neodymium to lutetium. The scheme in Figure 3 is identical for yttrium, holmium, erbium and lutetium as indicated by observed fragment ions and metastable peaks. However, for lutetium the metastable peak for loss of C_5H_5 from the parent ion is considerably weaker. In the scandium[69] and titanium[68] complexes no metastable peaks are observed for loss of C_5H_5 from the respective parent ions. For neodymium and samarium the low abundance of the $C_{11}H_{11}M^+$ fragment suggests that decomposition in the mass spectrometer *via* loss of acetylene as shown in Figure 3 is less favored for the early lanthanides. Also, only metastable peaks for loss of C_8H_8 and for loss of C_5H_5 can be confidently assigned. In Chapter III additional mass spectral data will be considered to see if this difference in decomposition pathway is still observed. Nevertheless, from the limited data here coupled with the infrared data it seems reasonable to suggest that the overall degree of electrostatic character in the metal-ligand bonding for the early lanthanides is somewhat higher than for the later lanthanides and yttrium.

iv) NMR Spectra

Attempts to obtain ^1H NMR spectra for the unsolvated complexes of neodymium, samarium, holmium, and erbium have so far proved unsuccessful. This is attributed to problems caused by low solubility of the complexes and the presence of the paramagnetic center within the complex. To date spectra have only been recorded for the yttrium and lutetium compounds. The data obtained are presented in Table 10 along with that for the scandium complex. An example of the ^{1}H NMR spectrum obtainable for the diamagnetic complexes is shown in Figure 4. The appearance of two sharp singlets is consistent with an η^{8}-C_8H_8 and η^{5}-C_5H_5 ligand bound to the metal. The chemical shifts for the carbocyclic ligands in both the yttrium and lutetium complexes are essentially equivalent and are in the expected region as judged by the scandium data.

The ^{13}C data obtained for the $(C_5H_5)Y(C_8H_8)$ complex deserves a few comments. As expected two resonances in an approximately 8:5 ratio were observed for this compound, the assignment of the resonances to the C_8H_8 and C_5H_5 rings being further secured by selective proton decoupling. It was noted however in the original spectrum, recorded at 15.08 MHz, that the signal due to the eight-membered ring was a doublet, the five-membered ring being observed as a sharp singlet. Since the yttrium nucleus has a nuclear spin of 1/2 in 100% natural abundance, the origin of the doublet was assigned to ^{89}Y-^{13}C coupling. To verify this assignment the spectra were recorded at 22.6 and 100.6 MHz. The doublet splitting remained constant

Table 10. NMR Data for $(C_5H_5)M(C_8H_8)^{a,b}$

M		^1H NMR(ppm)		^{13}C NMR(ppm)	
	Solvent	C_8H_8	C_5H_5	C_8H_8	C_5H_5
Y	Tol-d_8	6.25s	5.34s	93.4d[c]	108.1d[c]
Lu	Tol-d_8	6.24s	5.29s		
Sc[d]	CS_2	6.37s	5.13s		

[a] Chemical shift relative to TMS.

[b] s = singlet, d = doublet.

[c] $J_{^{89}Y-^{13}C_{(8)}} = 3.6$ Hz, $J_{^{89}Y-^{13}C_{(5)}} = 1.5$ Hz.

[d] Data from Ref. 69.

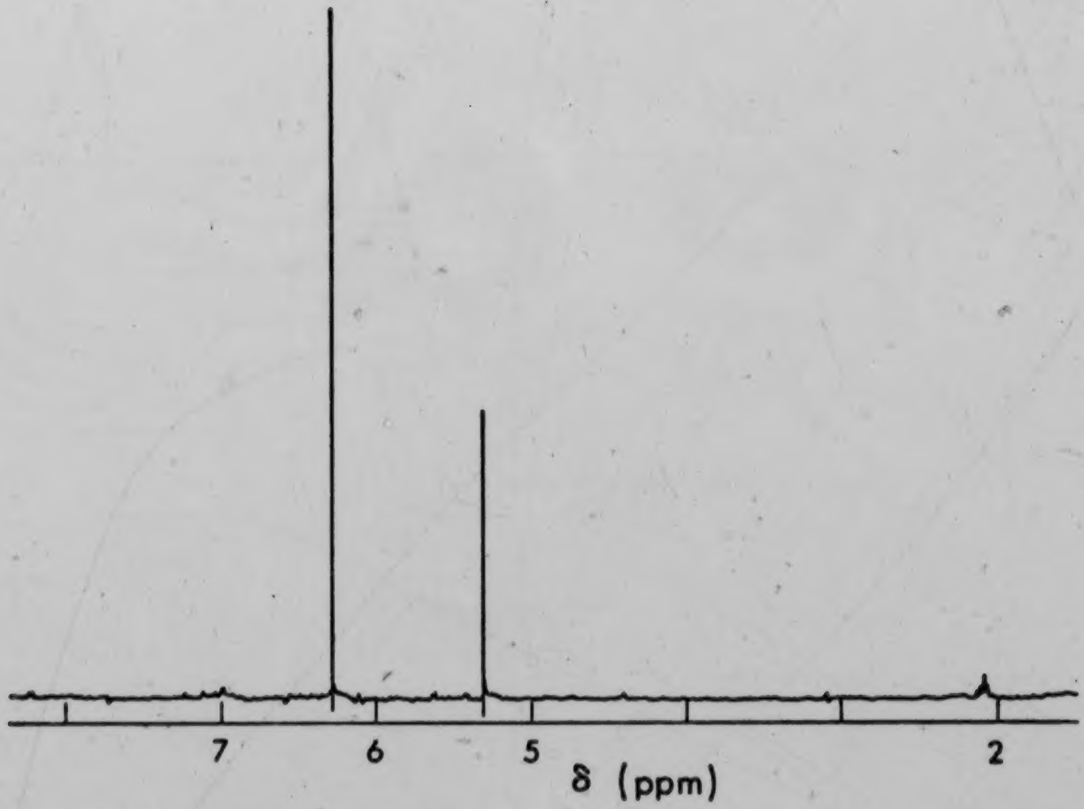


Figure 4: 100 MHz ^{1}H-FTNMR Spectrum of $(C_5H_5)Lu(C_8H_8)$ in toluene-d_8.

at 3.6 Hz. However, at 100.6 MHz the cyclopentadienide resonance was also a doublet with 1.5 Hz splitting. This is a very small value which is beyond the resolution of the other instruments and as a result the resonance appeared only as a singlet in the previous spectra. The coupling between ^{89}Y and ^{13}C is clearly demonstrated by these measurements. It is interesting to note that the magnitude of $J_{Y-C_8H_8}$ is greater than $J_{Y-C_5H_5}$. It is tempting to say that this observation further supports the speculation, presented in the infrared section, concerning the greater involvement of the C_8H_8 as opposed to the C_5H_5 ring M.O.'s with the metal ion. That the extent of metal-ligand bonding has important consequences on the magnitude of the coupling constant comes from a comparison with other known $J_{^{89}Y-^{13}C}$. The value is 28 Hz in $[Li(THF)_4][Y(CH_2SiMe_3)_4]$[45a] which contains an Y-C σ-bond, decreases to 12.2 Hz for the J_{Y-Me} in $[(C_5H_5)_2YMe_2AlMe_2]$[47] where electron deficient Y-C-Al bridge bonding exists, and is barely observable in the mixed sandwich complex where highly delocalized and largely ionic bonding predominates.

Finally the ^{13}C chemical shift data should be mentioned. Although data for analogous metal complexes for comparison is scarce, the chemical shifts of the rings are in the region expected for largely ionic cyclopentadienide and cyclooctatetraenide moieties.

4. Conclusion

The low solubility of the mixed sandwich complexes of the lanthanides and yttrium has limited investigation of their chemistry mainly to work in donor solvents which will be fully discussed in the following chapter, but from the data obtained it is possible to gain some insight into these compounds.

From the infrared and mass spectral data there appears to be an indication that early members of the lanthanide series differ from the later members and yttrium. This is also suggested by the greater difficulty in preparing the neodymium and samarium complexes. Similar difficulties were encountered by Dubeck[17] *et al.* when they were unable to synthesize the $(C_5H_5)MCl_2\cdot3THF$ complexes for the early lanthanides. It has been mentioned that the lanthanides have a strong tendency to obtain high coordination numbers so it is not unexpected that as the early, larger lanthanides are approached the balance of mainly electrostatic interaction and maximization of coordination number may become more delicate. Nevertheless, mixed sandwich complexes of the early and late lanthanide elements and of yttrium can be synthesized. The complexes appear to contain pentahaptocyclopentadienide and octahaptocyclooctatetraenide rings similar to those found in the analogous titanium and scandium complexes. Although, the solid state structure may involve additional, mainly electrostatic, interactions such that well separated monomeric units are not obtained. However, as shown by the structure of the $Nd(C_5H_4Me)_3$ complexes, these interactions should not significantly perturb the η^5- and η^8-bonding modes of the carbocyclic rings. Should this assumption be valid for the mixed sandwich complexes also, it seems reasonable to say that the data suggest a slight decrease in the overall degree of electrostatic character in the metal-ring bonding as one proceeds from the larger Nd^{3+} cation to the smaller Lu^{3+} cation.

The properties observed for the mixed sandwich complexes are quite similar to those of other organolanthanides containing these carbocyclic ligands and are in marked contrast to those of uranocene. Although our data has been interpreted to suggest some covalency in the bonding, there is, as yet, no evidence for significant metal-ligand covalent interaction in organolanthanides similar to the one which has been established for uranocene.

CHAPTER THREE

LEWIS ACID CHARACTER OF THE MIXED SANDWICH COMPLEXES $(C_5H_5)M(C_8H_8)$.

1. Introduction

The ability of the mixed sandwich complexes of the lanthanides and yttrium to function as Lewis acids was indicated in Chapter II by the initial isolation of tetrahydrofuran adducts prior to vacuum drying to produce the unsolvated species. This Lewis acidic behavior was not discussed for the analogous scandium and titanium complexes, but has been found and investigated for the tricyclopentadienide derivatives of the lanthanides[27,28,30-34]

It was thus of interest to investigate the scope of the Lewis acidic properties of the mixed sandwich complexes. In this chapter we will report on the range of Lewis bases that have been coordinated successfully to $(C_5H_5)M(C_8H_8)$ complexes and on the effect of adduct formation on the physical properties of the base free complexes. A comparison between the Lewis acidic behavior of the tricyclopentadienide and mixed sandwich derivatives of the lanthanide metals also will be given.

2. Synthesis

The preparation of the Lewis base adducts is straightforward as shown by the general equations.

$$(C_5H_5)M(C_8H_8) + \text{excess } L \xrightarrow[\text{R.T.}]{\text{Toluene}} (C_5H_5)M(C_8H_8)\cdot L \qquad \text{(III-1)}$$

$$(C_5H_5)M(C_8H_8)\cdot THF + \text{excess } L \xrightarrow[\text{R.T.}]{\text{Toluene}} (C_5H_5)M(C_8H_8)\cdot L + THF \qquad \text{(III-2)}$$

Direct reaction of the Lewis base (L) in toluene with the unsolvated mixed sandwich complex in toluene at room temperature produces the base adduct which can then be isolated by low temperature crystallization. Occasionally however, this yielded powdery or microcrystalline products instead of well formed crystals. In this manner representative compounds were prepared with the following bases: tetrahydrofuran (THF), pyridine (py), pyridine-d_5 (py-d_5) [as an aid in spectral identification], cyclohexylisocyanide ($C_6H_{11}NC$), and 1,10-phenanthroline (1,10-phen). Other bases attempted by this route that did not yield isolable adducts were: 2,3-dichloropyridine, triethylamine (NEt_3), diethylamine ($HNEt_2$), tri-n-butyl phosphine ($P(n\text{-}Bu)_3$), triphenylphosphine (PPh_3), dicyclopentadienyltin ($SnCp_2$), and triphenylphosphonium cyclopentadienylide ($\phi_3P\text{-}C_5H_4$).

Another base which has been investigated was ammonia. Dry ammonia was condensed onto the unsolvated mixed sandwich complex at liquid nitrogen temperature and the formed slurry was then kept stirring at -50°C for one to two hours. The excess amonia was boiled off leaving the base adduct which was further dried by passing a stream of dry nitrogen over the complex.

It was later found that the THF displacement route, eq (III-2), could equally well be applied to the synthesis of base adducts of the mixed sandwich complexes. This reaction also, works only with those bases which gave isolable adducts *via* eq. (III-1a). Although it was more convenient to work with excess ligand, the reaction with isocyanide and pyridine was carried out in several instances with stoichiometric amounts of the bases. The same adducts were isolated in these cases too. Thus the THF displacement is genuine and represents an apparent preference of the mixed sandwich complex for isocyanide and pyridine over the THF molecule. This is probably true for the other bases as well.

Because the THF adduct is now both precursor to the base free mixed sandwich complexes and starting material in the base displacement reaction (eq. III-2), the synthesis of this adduct was extended to the lanthanum, praseodymium, and ytterbium metals in addition to those listed in Chapter II. It was in the ytterbium reaction that a by-product formulated as $Yb_2(C_8H_8)_3$ was also isolated. This will be discussed in Chapter IV. Due to the very low solubility of the $Yb_2(C_8H_8)_3$ complex it was readily separated from the desired $(C_5H_5)Yb(C_8H_8)\cdot THF$. In the praseodymium and lanthanum reactions it became increasingly difficult to separate the desired mixed sandwich species from the by-products, and for lanthanum it was not possible to completely purify the mixed sandwich complex. A similar problem with the early lanthanides was alluded to in Chapter II where the low yields of neodymium and especially samarium mixed sandwich derivatives were mentioned. Nevertheless, the complexes can be prepared with varying degrees of difficulty in their purification.

The formulation of the base adducts as the mono-ligand derivative $(C_5H_5)M(C_8H_8)\cdot L$ is supported by elemental analysis, and in favorable cases by NMR data.

3. Results and Discussion

The Lewis acid-base adducts are, with the exception of the 1,10-phenanthroline adduct, moderately soluble in toluene. With 1,10-phenanthroline the maroon holmium adduct and green praseodymium complex precipitate from solution and are insoluble in all common organic solvents. Qualitatively the adducts appear to be somewhat easier to handle in the solid state than the base free mixed sandwich complexes but this is most probably due to the well formed crystals obtainable for the adducts which decompose more slowly than the microcrystalline or powdery base free complexes. The adducts are generally darker colored than the corresponding base free complexes (colors and analytical data will be found in Chapter VII). The change in color of the $(C_5H_5)Yb(C_8H_8)$ complex from deep blue to dark green upon formation of the cyclohexylisocyanide adduct is the most vivid example of this behavior.

i) Vibrational Spectra

It is clear from the detailed discussion given in Chapter II that the most significant features in the infrared spectrum of this type of complex are the appearance of three main bands in the 600-1600 cm^{-1} region assignable to the asymmetric C-C stretching [ν_a(C-C)], the in-plane C-H bending [δ(C-H)], and the out-of-plane C-H bending [γ(C-H)] modes of the C_5H_5 and C_8H_8 rings. The complete spectra will not be given here but only the bands noted above and pertinent vibrations arising from the base. Some complete spectra will be given in the experimental section of the final chapter for identification purposes.

We first consider the tetrahydrofuran adducts. Lanthanide complexes as well as their yttrium analogues readily form adducts with oxygen donors,[2] thus it is not surprising that the mixed sandwich complexes form THF adducts. In Figure 5 the spectra for holmium, yttrium, and neodymium complexes are compared. The general similarity between the early and late member of the lanthanide series is again apparent. The close correspondence for the yttrium complex again demonstrates its structural relation to these organolanthanide complexes. A comparison to Figure 1 shows that the spectra are very similar to the unsolvated complexes, the differences residing only in the appearance of additional bands due

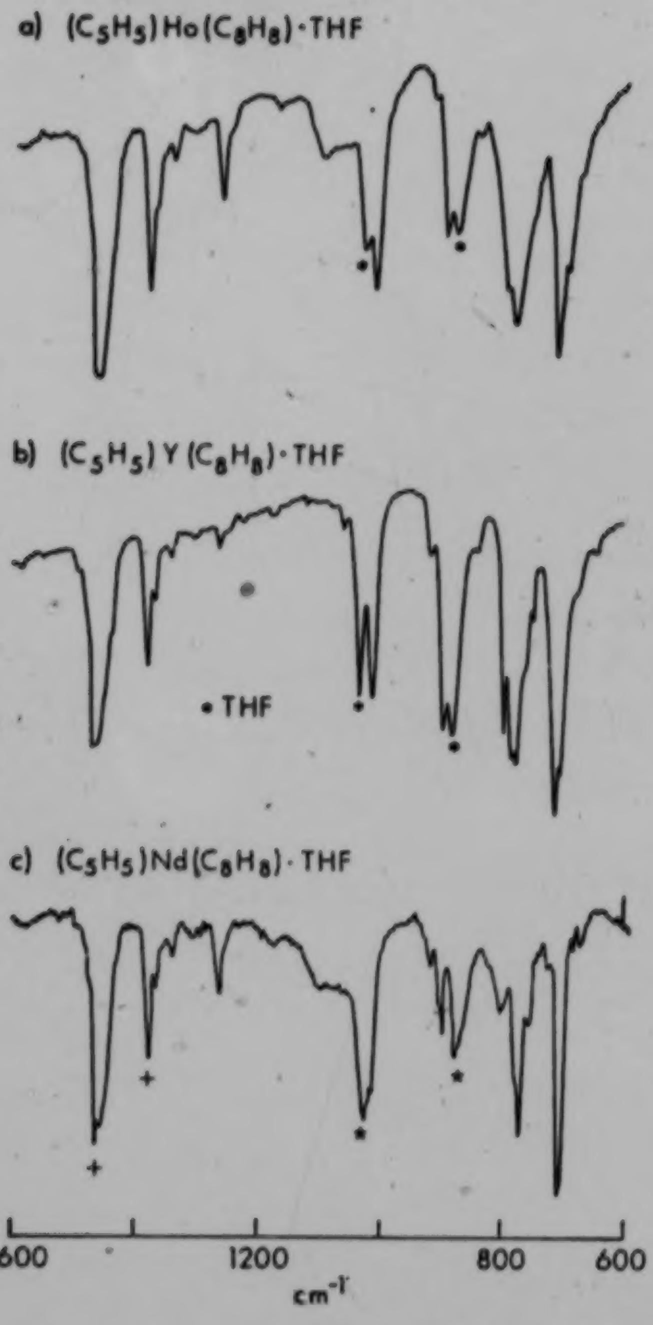


Figure 5: Infrared spectra of $(C_5H_5)M(C_8H_8)\cdot THF$ Complexes; M = Ho, Y, Nd. Recorded as mineral oil mulls. $^+$mineral oil.

to the base and small changes in the position of those bands that are sensitive to the metal-ring interaction. For this reason the spectra again indicate an η^5-C_5H_5 and η^8-C_8H_8 bonding mode for the carbocyclic rings. Table 11 lists the position for the assigned frequencies plus two characteristic vibrations due to the tetrhydrofuran ligand.

The difficulty in purifying the lanthanum derivative was mentioned above and leads to difficulties in obtaining a clean spectrum. By recrystallizing the complex from tetrahydrofuran the bands assignable to by-products decreased in intensity but could not be eliminated. The γ(C-H) region for the C_5H_5 ring always appeared too strong and too broad, thus the band positions for the lanthanum complex are not given in Table 11. For the remaining complexes no such problem occurred.

Having made the conclusion in Chapter II that there is a substantial electrostatic component in the metal-ring bonding which is reflected in the low frequency of the out-of-plane C-H bending mode for the rings, it is now possible to consider the effect of coordination of THF on these bands. It would be reasonable to assume that as the mixed sandwich complex forms a Lewis base adduct the amount of electron density required from the other ligands to satisfy the electronic demand of the metal ion should decrease resulting in more ionic metal-ring

Table 11. Major Bands in the Infrared Spectra of $(C_5H_5)M(C_8H_8)\cdot THF^{a,b}$

M	Assignment						
	C_8H_8			C_5H_5			THF
	ν_a(C-C)	δ(C-H)	γ(C-H)	ν_a(C-C)	δ(C-H)	γ(C-H)	
Pr	1435w-m	894m	700s/689s	1435w-m	1010s	773s/764s	1023s, 873m
Nd	1436w-m	897m	704s/695s	1436w-m	1010s	778s/768s	1023s, 870m
Y	1439m	898s	712s/705s	1439m	1012s	788s/780s	1035s, 881s
Ho	1438m	897m-s	714s/697s	1438m	1012s	798s/781s	1030s, 880m
Er	1438m	893m-s	708s/692s	1438m	1012s	788s/780s	1031s, 876m
Yb	1438m	897m	711s/691s	1438m	1015s	782s,br	1033s, 880m
Lu	1438m	899m	720s/712s	1438m	1015s	797s/787s	1034s, 882m

[a] Spectra recorded as mineral oil mulls; frequencies in cm^{-1}.

[b] Abbreviations: br = broad; band could not be resolved into two components.
s = strong; m = medium; w = weak.

bonding. Comparison of the data in Table 11 with that for the respective unsolvated complex in Table 3 generally reflects this expectation. It is seen that, with the exception of the lutetium derivative, the frequency of the out-of-plane C-H bending mode of the C_8H_8 ring decreases by approximately 15-20 cm^{-1} upon adduct formation. Interestingly however, the analogous vibrational mode for the C_5H_5 ring remains relatively constant.

It thus appears that the bonds between the metal and the cyclic ligands retain their ionic character and if anything, for the complexes up to erbium, are more ionic in the THF adduct than in the base-free mixed sandwich complex. This same effect of increasing degrees of ionic character upon adduct formation with a Lewis base was demonstrated for $Ca(C_5H_5)_2$ and its THF adduct.[77] It is interesting that the spectral changes and the implied charge variations on the rings are what would have been predicted based on the speculative ideas presented in Chapter II concerning the bonding in these complexes. It was shown that the most probable metal-ring interactions are between the metal 6d ($d_{x^2-y^2}$, d_{xy}) and the e_2 M.O. of the C_8H_8 ring. Adduct formation should perturb this interaction the most causing electron density to flow back onto the C_8H_8 ring, the charge on the C_5H_5 moiety being less affected.

The bands shown in Table 11 for THF are attributed to ring stretching vibration[77,85] and are the most sensitive to coordination. They occur at 1067 and 908 cm^{-1} respectively in free THF. The decrease in frequency of these vibrations in the adducts represents a significant but relatively weak M-O interaction. The highest frequency band usually shifts by 40-100 cm^{-1}, the value observed here of ca. 40 cm^{-1} being at the lower end of this range. These bands in the praseodymium and neodymium complexes appear at lower frequency than for the later lanthanides and yttrium as seen in Table 11. This greater preference for the oxygen ligand in the early lanthanide members may reflect increased hardness of the metal center relative to the later entries of the Table, some structural change, or it may simply be a reflection of the decreased ligand-ligand repulsion created by the larger size of the lighter lanthanides. Unfortunately the frequencies of these vibrations are not generally available for the THF adducts of the tricyclopentadienide derivatives of the lanthanides which would permit a comparison of the Lewis acid strength for the two types of organolanthanide complexes. However in the $Cp_3Yb{\cdot}THF$[24,27] complex the bands at 960 and 838 cm^{-1} are apparently due to THF. This would indicate a stronger Yb-O interaction than in the analogous mixed sandwich complex where the bands are at 1033 and 880 cm^{-1}. This of course is not sufficient to make a general statement about the relative strengths of the two classes of Lewis acids. Although, the relatively easier removal of coordinated THF from the mixed sandwich complexes is in accord with the above conclusion. It should be possible to get this information by extending the data to additional bases common to the two series. Because Eq (III-2) shows that some bases can readily replace THF the data should also reflect this greater base strength relative to THF by further lowering the frequency of the out-of-plane C-H bending modes.

In Table 12 are collected the data for the cyclohexylisocyanide, pyridine, ammonia and 1,10-phenanthroline adducts. This represents the types of base adducts that have been isolated and will be further discussed below when considering the reactivity of the mixed sandwich complexes.

The cyclohexylisocyanide adducts were also extensively investigated. The reason for this is twofold. The adducts represent interesting examples of organolanthanide complexes because there exists a lanthanide to carbon σ-bond in addition to the symmetrical metal-ring bonding. Furthermore the base has been found to complex strongly to the tricyclopentadienide derivatives of the lanthanides and yttrium.[27,28] Since the infrared spectra of these adducts have been reproted, a meaningful comparison of the Lewis acid strengths of the tricyclopentadienide and mixed sandwich complexes of the lanthanides is also possible. The

Table 12. Major Bands in the Infrared Spectra of $(C_5H_5)M(C_8H_8)\cdot L^{a,b}$

M	L	C_8H_8			C_5H_5			L
		ν_a(C-C)	δ(C-H)	γ(C-H)	ν_a(C-C)	δ(C-H)	γ(C-H)	
Pr	$C_6H_{11}NC$	1432w	895m	698s/672s	1432w	1015s	777s,br	2190m, 1369m-w
Sm		1438w	897m	701s/695s	1438w	1015s	768s/757s	2180m, 1367m-w
Y		1440m	898m	708s/698s	1440m	1014s	776s/770s	2193m,1463m,1367m-w
Ho		1438m	897m	709s/700s	1438m	1011s	788s/774s	2192m,1462m,1350m-w
Er		1440m	898m	709s,br	1440m	1015s	789s/775s	2194m,1463m,1364m
Yb		1436m	898m	704s/699s	1436m	1015s	785s/770s	2186m,1463m,1365m
Nd	C_5H_5N	-	895m	708s/695s	-	1010s	799br,s	1590s,1440s,1036s
Sm		-	896m	707s/701s	-	1003s	792s/772s	1595s,1439s,1035s
Y		1436m	897m	712s/708s	1436m	1008s	782s/770s	-
Ho		1433m	897m	709m-s/703s	1433m	1009s	782s/772s	1602s,1445s,1037s

continued......

Table 12 (continued)

M	L		C_8H_8			C_5H_5		L
		ν_a(C-C)	δ(C-H)	γ(C-H)	ν_a(C-C)	δ(C-H)	γ(C-H)	
Nd	NH_3	1440w-m	897s	703s,br	1440w-m	1010m	790s/773s	3335w,3245w,1586m-s, 1216,1138m
Ho		1438m	897s	712s/698s	1438m	1009s	791s/771s	3320w,3240w,1595m-s, 1230s,1160m
Ho	1,10-phen.	1445m	898m	715s/703s	1445m	1013s	781s/772s	

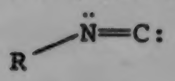
[a] Spectra recorded as mineral oil mulls; frequencies in cm^{-1}.

[b] br = broad; band could not be resolved into two components.

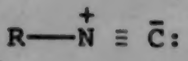
s = strong, m = medium, w = weak.

strength of adduct formation with the $M(C_5H_5)_3 \cdot CNC_6H_{11}$ complexes is evidenced by their ability to sublime unchanged at 150-160°C. Within the mixed sandwich complexes it is found that the cyclohexylisocyanide can be removed by vacuum drying below 100°C, and that none of the complexes sublimed as the cyclohexylisocyanide adduct. In the samarium case vacuum drying for 18-20 hours at room temperature removed the base as evidenced by disappearance of the C-N stretching frequency, ν(C-N), at 2180 cm^{-1}. Stronger metal-isocyanide bonding in the case of the tricyclopentadienide complexes is clearly indicated by these observations.

A different way of assessing the relative strength of metal-isocyanide interaction comes from the analysis of the infrared spectra of the complexes in the C-N stretching region. One way this can be understood is to consider the free ligand to be a hybrid of forms A and B. Although the free isocyanide is bent indicating a predominance of form A, upon coordination to a Lewis acid form B and a linear isocyanide moiety is usually favored.[86] In the absence of complications arising from strong back donation from the metal into empty π* M.O's of the base, the increase in ν(C-N) upon adduct formation thus reflects



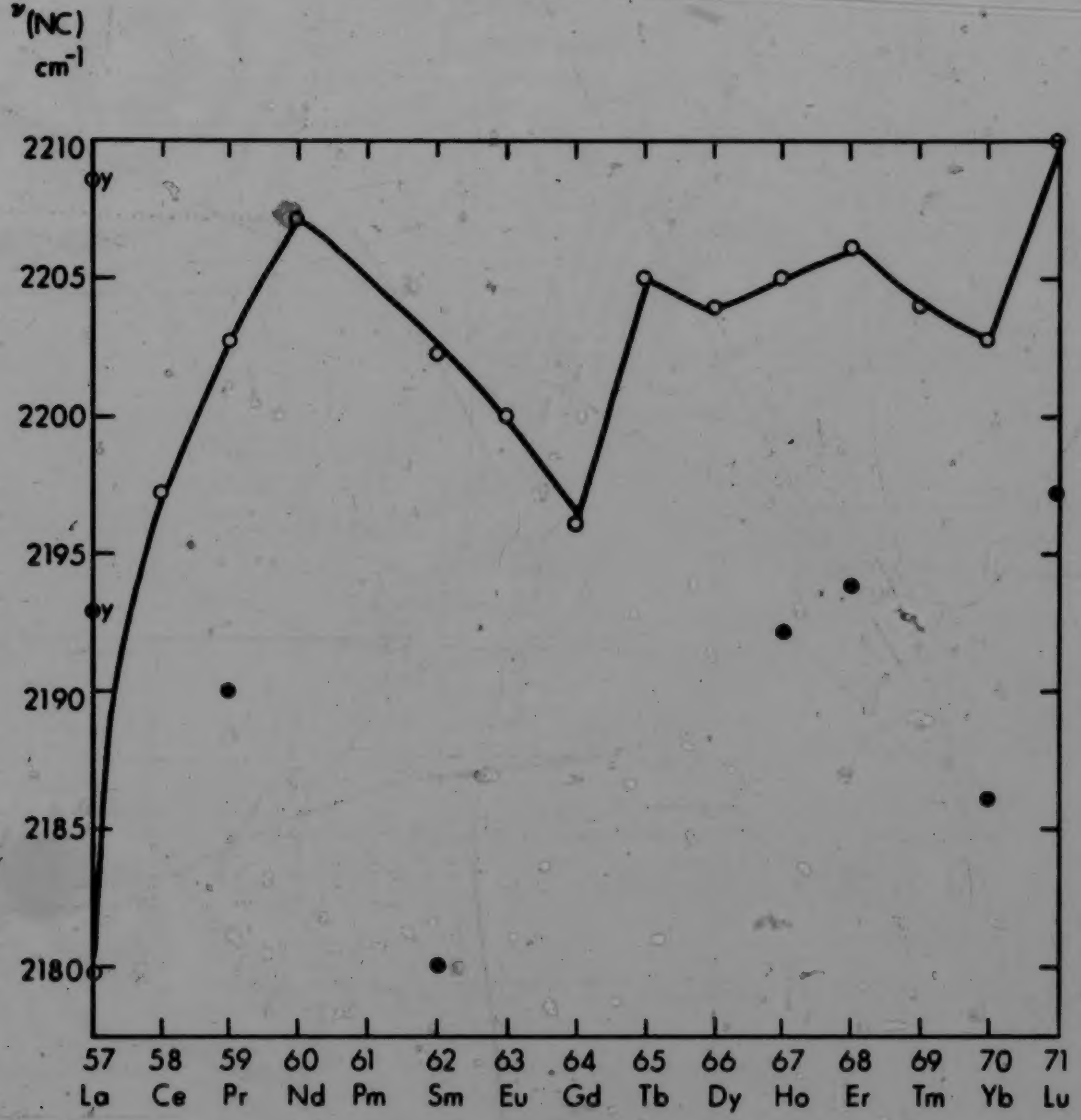
A



$R-\overset{+}{N}\equiv\bar{C}:$

B

the increased importance of form B and consequently gives a measure of the strength for the metal-CNR interaction.[87] For Lewis acids containing boron, aluminum and the lanthanides, the isocyanide is expected to behave as a pure σ donor and the simple correlation just mentioned between ν(C-N) and metal-CNR bond strength should hold. Fischer and Fischer[27] in their study on $(C_5H_5)_3M\cdot CNC_6H_{11}$ complexes have treated the interaction as one due to purely σ-donation from the base. This study was extended by von Ammon and Kanellakopulos[28] to include, with the exception of promethium, all lanthanide tricyclopentadienide complexes. The variation in ν(C-N) in the $(C_5H_5)_3M\cdot CNC_6H_{11}$ complexes can be seen in Figure 6. The observation of the so called tetrad effect is interpreted by von Ammon as an indication of partial covalent character of the M-C bond. In addition an analysis of the paramagnetic shifts of the C_6H_{11} protons apparently indicates a small bending of the isonitrile group. Based on these two observations the possibility of f → π^* back bonding in these adducts was raised by these two researchers. However, a single crystal X-ray diffraction study for the praseodymium[88] complex indicates an essentially linear isocyanide, C-N-C angle of 177.8 (1.6)°, with C-N bond length of 1.11 Å which is consistent with the presence of a C-N triple bond. The structure clearly favors form B with the isocyanide functioning as a pure σ-donor group.



Atomic Number

Figure 6: Stretching Frequency, $\nu_{(NC)}$ for cyclohexyliso-cyanide Adducts:

$[M]\cdot CNC_6H_{11}$

$[M] = M(C_5H_5)_3$[a]; represented as o

$[M] = (C_5H_5)M(C_8H_8)$; represented as ●

Free $C_6H_{11}NC$; $\nu_{(NC)} = 2138$ cm^{-1}

---

a) Data taken from and displayed as in Ref. 28.

Irrespective of the minor subtleties in metal-carbon bonding it is evident that the base is acting primarily as a σ-donor, thus the relative acid strength of these organolanthanide complexes can be obtained based on the ν(C-N) frequency of the isocyanide ligand in the adducts.

The C-N stretching fequencies of the mixed sandwich adducts are also presented in Figure 6. The frequencies in every case are lower than those for the corresponding tricyclopentadienide adducts. This again indicates a stronger lanthanide to isocyanide carbon bond in the latter complexes.

An examination of Figure 6 also reveals an interesting variation in ν(C-N) as the lanthanide metal is changed. Although our data are not as extensive as for the $(C_5H_5)_3M\cdot CNC_6H_{11}$ complexes and it is not yet apparent whether a variation paralleling that observed by von Ammon *et al.*[28] will be obtained, it is clear that the increase in stretching frequency upon proceeding from praseodymium to lutetium is broken at samarium and ytterbium. A possible explanation for this may lie in the availability of the relatively stable 2+ oxidation state for these lanthanide metals. The presence of reducing carbocyclic ligands coupled with the easily accessible 2+ oxidation state can be said, in a simplistic and qualitative analysis, to produce more M(II) "character" of the lanthanide ions in the Sm and Yb complexes than in the other compounds.

Since the M(II) ion is less polarizing than the M(III) ion the resulting metal-ligand interactions are expected to be weaker. This is reflected in the low ν(C-N) isocyanide frequencies. The lower than "expected" values that are often, although not consistently, observed for the out-of-plane C-H bending modes for the C_5H_5 and C_8H_8 rings with these two metals (Tables 11, 12) also tend to support the above suggestion.

Inspection of Tables 11 and 12 also reveals that, as observed in Chapter II, there seem to be increases in the frequency of the out-of-plane C-H bending modes of both C_8H_8 and C_5H_5 rings proceeding from praseodymium to lutetium, or more appropriately it may be said that the frequency of these vibrations on the whole is lower for the lighter lanthanide complexes (Pr, Nd, Sm) than for the heavier lanthanide mixed sandwich derivatives (Ho, Er, Yb, Lu). This, as suggested in Chapter II, is in keeping with the expected slight decrease in the overall electrostatic character of the metal-ligand bonding for the latter compounds.

The last point to consider for the isocyanide adducts relative to the respective tetrahydrofuran adducts is whether the infrared data in Tables 11 and 12 correlate with their apparent differences in base strength toward the mixed sandwich complex. Since the THF was replaced by the stronger σ-donor, $C_6H_{11}NC$ in this case, the lanthanide ion requires less electron density from the carbocyclic rings in the isocyanide adducts and this should be reflected in lower values for the out-of-plane C-H bending modes. This mode (empirically demonstrated in Chapter II)[73] is sensitive to the amount of electron density in the ring, decreasing in frequency as the electron density increases. Reference to Tables 11 and 12 shows that, although this seems to be borne out in general (γ(C-H) for the C_5H_5 ring of Pr and Yb being the exceptions), the changes in frequencies are rather small and at the threshold of chemical significance. This of course is not very surprising. We have already observed that the changes in the γ(C-H) modes upon THF adduct formation although detectable for the C_8H_8 ring were minimal for the cyclopentadienide moiety. Since adding a base to the unsolvated complex certainly produces a more drastic electronic change in the complex than replacing one base by another, the changes in frequency of the γ(C-H) modes for the rings are expected to be smaller for the latter case. This is seen from the data in Tables 11 and 12. It is clear that because of the small changes, a ranking of the bases according to their base strength toward the mixed sandwich complexes based on the position of these vibrations is not feasible. Indeed it is interesting to note that an oxygen donor function (THF) can be displaced by carbon (CNR) and nitrogen (Py, NH_3, 1,10-phen) bases in the present complexes. The preference of the hard lanthanide ions for oxygen ligands is well recognized, the present observation with the mixed sandwich complexes points again to the increased softness of the complexes when reducing, highly polarizable carbocyclic ligands are present.

The few nitrogen base adducts listed in Table 12 were prepared only in order to see whether some nitrogen donor ligands could effectively compete for a coordination site on the mixed sandwich complex. A detailed discussion of their infrared spectra, comparable to that for THF and CNC_6H_{11} adducts, will not be given due to the paucity of data.

The assignment of the characteristic base vibrations was done by comparison to literature values. Gill *et al.*[89] have looked at the spectra of numerous pyridine complexes noting that most of the bands remain constant in the 600-1600 cm^{-1} region with the exception of the band in free pyridine at 1578 cm^{-1} which shifts towards 1600 cm^{-1} upon complex formation. The three bands shown for pyridine vibrations in Table 12 are moderately strong to strong bands which are easily observed and the band near 1600 cm^{-1} is typical of coordinated pyridine. For the ammonia adducts the ligand vibrations also are as expected. The N-H stretching frequencies in free ammonia occur at 3414 and 3336 cm^{-1} and experience a decrease upon coordination.[90] This is as observed in both Nd and Ho complexes. Again the remaining vibrations are strong ligand vibrations which permit easy characterization of coordinated ligand as these appear in regions typical of complexes involving ammonia.[91] For 1,10-phenanthroline the bands due to the ligand are too numerous to list.

Examination of the characteristic ring vibrations listed in Table 12 for these adducts reveal that although the band positions tend to support the conclusions so far reached based on infrared data, there are a few anomalies relative to the trends we have tried to establish. For all of the adducts, the out-of-plane C-H bending mode for the C_8H_8 ring is at lower frequency than in the unsolvated complexes, Table 3. This is also true for the C_5H_5 ring except in the neodymium complex with ammonia where there is no change and in the pyridine adduct where the frequency is apparently higher (799 br) than in the base free complex (789/772). However in this last case the broadness of the band in the pyridine adduct makes comparison tenuous. The higher γ(C-H) frequency of the C_5H_5 ring observed in the neodymium ammonia adduct than in the corresponding THF adduct also is not as expected based on the displacement of coordinated THF by ammonia. No explanation can be offered for these observations.

It might be good to emphasize at this point that in addition to the above mentioned anomalies a few other exceptions to the trends in the infrared data can also be found in the frequencies listed in the Tables. Some of these reflect subtleties of the lanthanide ions themselves (Sm, Yb). Some are unexpected (ex. low frequency of the γ(C-H) mode in the Er compounds) and for these we have no explanation to offer. Nevertheless, we believe that the great majority of the data lend credence to the trends discussed.

To complete the picture obtainable from vibrational data, Raman spectra for the complexes could be informative. Raman data for organolanthanide complexes are not extensive. This is partly due to the propensity of the lanthanides to fluoresce thus causing problems in obtaining clear spectra. This problem was also encountered in this study for most of the lanthanide complexes. The compounds for which spectra were obtained are given in Table 13 together with data for related compounds.

The Raman spectra of the complexes consist of two strong bands at ~1120 and ~750 cm^{-1} in addition to a complicated, multiple absorption region from 300 to 200 cm^{-1}. The bands at 1120 and 750 cm^{-1} can be assigned confidently to the symmetric ring breathing modes of the C_5H_5 and C_8H_8 rings respectively.[92,93,11] Assignment in the low frequency region is not possible. Reference to the ruthenocene and uranocene data in the Table reveals

Table 13. Raman Spectra[a] of $(C_5H_5)M(C_8H_8)$ Complexes in the 1200-190 cm^{-1} Range.[a]

$(C_5H_5)Er(C_8H_8)\cdot THF$	$(C_5H_5)Lu(C_8H_8)\cdot THF$	$(C_5H_5)Y(C_8H_8)$	$K[Ce(C_8H_8)_2]$[b]	$Nd(C_5H_5)_3$[c]	$U(C_8H_8)_2$[b]	$Ru(C_5H_5)_2$[d]	Assignment[e]
1130m-s							
				1126vs			
1115s	1119s	1121m-s					
				1120s			
						1098s	ν_s(C-C),C_5H_5
						1060m	
903w							
		802w					
				780m			
						815m	
				765m			
753vs	741s	751s	750m				
					750m		ν_s(C-C),C_8H_8
	367w	372w	370m				
					380w	396m	
	351w	363w					
						325s	ν(M-C_5H_5)
280s		274vs					
268s							
261s	260w-m	260m-s					
				260m-s			
f	241w-m						
				247m-s			
		236m-s		230m-s			
	218w-m	225vs	200s				
					215s		ν(M-C_8H_8)
		195vs		192m			

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[a] Spectra recorded here on solids sealed *in vacuo*; frequencies in cm^{-1}; vs = very strong, s = strong, m = medium, w = weak.

[b] Ref. 11. [c] Ref. 92. [d] Ref. 93. [e] Assignments are those for the compounds in Refs. 11,92,93.

[f] Low frequency region obscured by steep rise in baseline upon approaching the exciting line.

that this region is associated with metal-ring stretching vibrations. The expectation for an isolated $(C_5H_5)M(C_8H_8)$ molecule would be the appearance of the symmetric and asymmetric metal-ring stretch in this region. The actual spectra contain several additional bands. The low frequency Raman region of $Nd(C_5H_5)_3$ is also complicated perhaps because of association in the solid state which has already been mentioned. It is possible that complexity of the spectrum of the mixed sandwich compound is also related to such behavior. At any rate, the appearance of bands in the region normally associated with metal-ligand skeletal vibrations also suggests some metal-ring covalent interactions.

ii) Mass Spectra

Table 14 displays the major metal containing fragments observed for the base adducts of the mixed sandwich complexes. The first thing to notice is that the parent ion is usually not observed. This is not entirely unexpected since the infrared data and physical properties of the compounds so far presented did suggest relatively weak metal-donor interaction. As we have seen before the $C_{13}H_{13}M^+$ ion, the fragment resulting from the loss of the Lewis base from the parent molecule, is more intense for the heavier lanthanides than for the lighter members of the series. It also appears that for the former

Table 14. Relative Abundance for Major Metal Containing Fragments in the Mass Spectra of $(C_5H_5)M(C_8H_8)\cdot L^{a,b}$

M	L	$C_{13}H_{13}M\cdot L^+$	$C_{13}H_{13}M^+$	$C_{11}H_{11}M^+$	$C_8H_8M^+$	$C_5H_5M^+$	C_2HM^+	M^+	Source Temperature
Pr	THF	-	37	-	33	100	13	14	120°
Nd	THF	-	40	-	89	100	13	20	170°
Nd	py	-	59	-	100	82	13	23	170°
Sm	THF	-	24	-	2	100	6	23	120°
Y	THF	-	100	10	65	48	7	7	65°
Y	py-d_5	<.1	100	6	55	49	9	5	155°
Y	$C_6H_{11}NC$	.7	100	11	63	40	12	4	165°
Ho	THF	-	100	4	49	55	10	24	125°
Ho	$C_6H_{11}NC$	~.1	100	3	41	56	11	25	85°
Er	THF	-	100	6	44	45	6	16	75°
Er	$C_6H_{11}NC$	.2	100	7	39	43	7	16	85°
Yb	THF	-	24	-	5	100	11	52	100°
Lu	THF	-	100	11	23	72	7	16	100°

[a] Ionizing voltage = 70 eV. [b] THF = tetrahydrofuran, py = pyridine.

complexes, with the exception of Yb, this peak is also the most abundant metal containing fragment whereas for the latter complexes it is the $C_8H_8M^+$ or $C_5H_5M^+$ ions that are the most abundant. The anomalous mass spectral behavior of Yb is attributed to the relatively stable 2+ oxidation state of the metal, which favors fragmentation *via* the neutral C_8H_8Yb moiety and as the $C_5H_5M^+$ ion where the ytterbium has the preferred 2+ formal oxidation state. This then accounts for the weak $C_8H_8M^+$ but very strong $C_5H_5M^+$ ions in the mass spectrum of the complex. The weak $C_{13}H_{13}M^+$ ion could also be a consequence of this tendency of Yb toward the 2+ oxidation state. Similar arguements also hold for the base free and THF adduct complexes of samarium which also has a stable 2+ oxidation state.

Inspection of the table also reveals that besides the two metals mentioned above, for the remaining mixed sandwich adducts both $C_5H_5M^+$ and $C_8H_8M^+$ moieties are important fragment ions, although there are variations in relative abundance of the respective peaks for which we have no explanation. As pointed out in Chapter II already this observation is contrary to mixed sandwich complexes of the transition metals where the $C_8H_8M^+$ ion is in considerably lower abundance than the $C_5H_5M^+$ fragment.

Regarding the fragmentation patterns for the adducts, they do not provide new decomposition routes when compared to the respective unsolvated complex. In particular the cyclohexylisocyanide adduct exhibits the same metastable peaks as in Figure 2 with one additional metastable peak for the fragmentation below:

$$(C_5H_5)Ho(C_8H_8)\cdot CNC_6H_{11}^{+} \xrightarrow[m^*=251.8]{-CNC_6H_{11}} (C_5H_5)Ho(C_8H_8)^{+} \tag{III-3}$$

This was the first direct observation of the parent ion for the base adduct. An additional demonstration that it behaves as the molecular ion is shown in Table 15. It is typical to observe the relative increase of the parent molecular ion at the expense of the breakdown fragments as the ionizing voltage is lowered.[94] This is aptly demonstrated by the data in Table 15 for the isocyanide adduct of holmium and the pyridine-d_5 adduct of yttrium.

We thus see that the mass spectra for the base adducts reflect the same differences between the early lanthanides and the later members of the series and yttrium that were discussed for the mass spectral data in Chapter II. That is, the interaction between the carbocyclic rings and the metal appears to be stronger for the later members of the lanthanide series.

Table 15. Effect of Ionizing Voltage on Parent Ion in $(C_5H_5)M(C_8H_8)\cdot L^{a,b}$

M	L	Ionizing Voltage	$C_{13}H_{13}M\cdot L^+$	$C_{11}H_{11}M^+$	$C_8H_8M^+$	$C_5H_5M^+$
Ho	$C_6H_{11}NC$	70 eV	.1		74	100
		20 eV	.8		162	100
		12 eV	277		123	100
Y	C_5D_5N	70 eV	.1	100	911	820
		20 eV	.6	100	c	c
		16 eV	1.9	100	c	c
		14 eV	13	100	300	19
		12 eV	916	100	425	208

[a] Values are relative to a constant of 100.

[b] Data taken at constant temperature, T = 110°C, Y; T = 160°C, Ho.

[c] Peaks off scale.

iii) NMR Spectra

The lack of success mentioned in the previous Chapter in recording the ^{1}H NMR spectra of many of the mixed sandwich complexes of the lanthanides persisted with the base adducts also. In addition to the diamagnetic complexes of Y and Lu, the only paramagnetic derivatives that gave recognizable signals for the carbocyclic ligands were those of Nd and Sm.

The data obtained are collected in Table 16 together with the unsolvated complexes for comparison. As shown in Figure 7 the resonances observed for the diamagnetic compounds were always sharp singlets and remained invariant over the temperature range -40 to +60°C, which is consistent with the symmetrical octahapto and pentahapto bonding modes for the C_8H_8 and C_5H_5 rings respectively. Although the ^{1}H NMR spectra of the THF adducts were obtained in pyridine-d_5, thus displacing THF, the spectra nevertheless provide convenient verification for the presence of one THF molecule in these complexes.
This is shown in Figure 8 which includes the integration of the respective peaks and also by the relative intensities of the ligand resonances listed in the table. A reference to the table shows that the relative intensities for the isocyanide ligand are slightly larger than expected for one coordinated ligand molecule. This is

Table 16. Proton NMR data for $(C_5H_5)M(C_8H_8)\cdot L$ Complexes[a]

M	L	Solvent	C_8H_8[b]	C_5H_5[b]	L
Lu	-	toluene-d_8	6.24	5.29	
Lu	-	pyridine-d_5	6.21	5.50	
Lu	THF	pyridine-d_5	6.20	5.48	3.59(4H,m),1.54(4H,m)
Lu	$C_6H_{11}NC$	toluene-d_8	6.19	5.48	2.23(1.3H,m),0.91(13H,m)
Y	-	toluene-d_8	6.25	5.34	
Y	-	pyridine-d_5	6.29	5.61	
Y	THF	pyridine-d_5	6.28	5.61	3.64(4H,m), 1.59(4H,m)
Y	$C_6H_{11}NC$	toluene-d_8	6.24	5.57	2.28(1.2H,m),0.98(12H,m)
Nd	THF	pyridine-d_5	0.87[c]	2.79[c]	3.65(4H,m),1.62(4H,m)
Sm	THF	DMSO-d_6	7.48[d]	5.98[d]	3.68(4H,m),1.72(4H,m)

[a] Chemical shifts (δ) in ppm from TMS by appropriate conversions from internal solvent references.

[b] All C_8H_8 and C_5H_5 resonances are of intensity 8 and 5 respectively and, with the exception of Nd and Sm, are sharp singlets.

[c] Width at half-height: C_8H_8 = 40 Hz, C_5H_5 = 28 Hz. [d] Width at half-height: C_8H_8 = 5 Hz, C_5H_5 = 2 Hz.

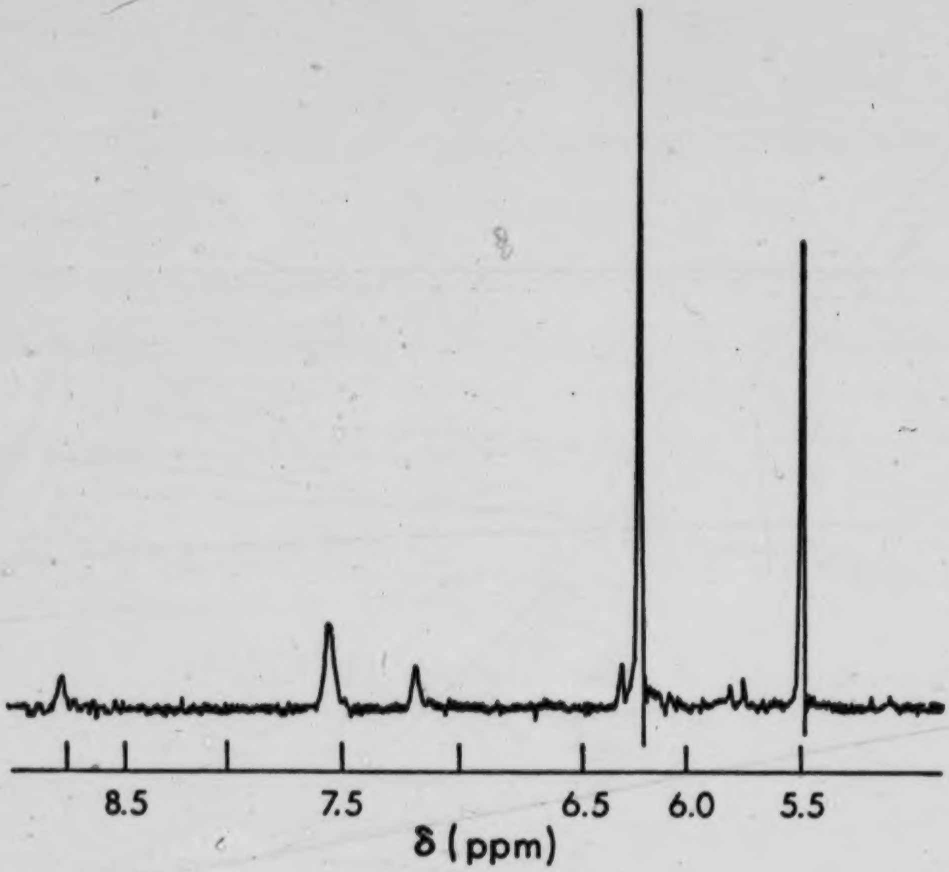


Figure 7: 90 MHz ^{1}H-NMR spectrum of $(C_5H_5)Lu(C_8H_8)$ in pyridine-d_5.

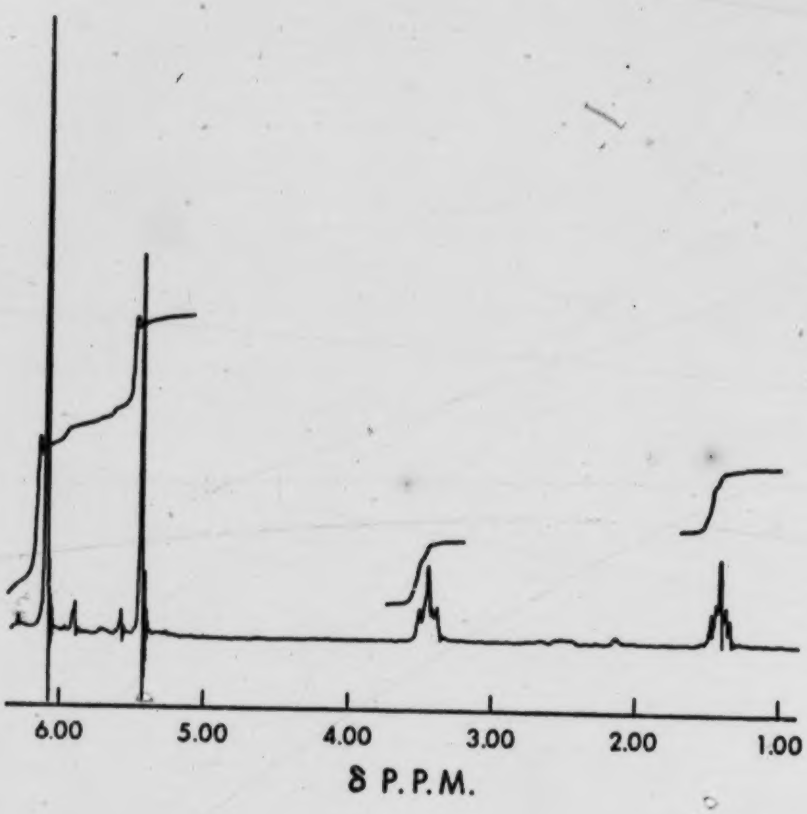


Figure 8: 100 MHz ^{1}H NMR of $(C_5H_5)Y(C_8H_8)\cdot THF$ in pyridine-d_5.

attributed to the difficulties experienced in handling these adducts. It was pointed out that vacuum drying is capable of removing the coordinated base. Thus, the isolation of the base adducts often involves filtration and drying under a stream of nitrogen. Since cyclohexylisocyanide has a high boiling point, residual free ligand could remain with the desired product causing the errors in the integrations.

The chemical shift data of the diamagnetic compounds, although potentially useful in obtaining information about the charge density on the carbocyclic rings, has proved difficult to interpret satisfactorily. Before commenting on the data a brief summary of the ^{1}H NMR data in predominantly ionic cyclopentadienide and cyclooctatetraenide complexes will be highlighted.

In a careful NMR study Jackman *et al.*[95] have investigated the effect of ion pairing of carbanions on their chemical shifts. For contact ion pairs it is anticipated that the chemical shift of the anion will be at highest field with the largest cation since this is the case where the effective charge on the anion is the largest. Although for the alkali metal cyclopentadienides the chemical shifts roughly followed the above expectation in ether solvents and thus gave indication of the existence of contact ion pairs, the situation was complicated by the dependence of the chemical shifts on temperature and concentration[96] (NaC_5H_5 in THF, δ5.57 for a 1.0 M solution and 5.72 when the concentration is reduced to 0.01 M). Concentration dependent aggregate formation and/or equilibria between contact and solvent-separated ion pairs were postulated to account for the complications. The ^1H NMR spectra of $Ca(C_5H_5)_2$ and $Mg(C_5H_5)_2$ were not concentration dependent, the slight change of the chemical shifts in THF, δ5.75 and δ5.82, on going from Na to Ca and then to Mg is in apparent accord with the presence of contact ion pairs.[77] This argument could also be extended to $Lu(C_5H_5)_3$ where the higher effective nuclear charge on the metal would predict an even lower field absorption, the observed value of δ5.90 in THF is in line with this. However, there are some unexpected results. Allan *et al.*[77] have found an unexpectedly large downfield shift of the cyclopentadienide resonance in $Ca(C_5H_5)_2$ when dissolved in pyridine (δ6.29), specific interaction between polar solvent and solute was given as a reason for the observation. The chemical shift of $Lu(C_5H_5)_3$ however did not change with solvent, δ5.83 in THF and 5.90 in C_6D_6.

The ^1H NMR spectra of alkali metal cyclooctatetraenide complexes were recorded by Cox *et al.*[97] In diethyl ether the protons were shielded in the order Rb > K > Na > Li, suggesting the presence of contact ion pairs, whereas in in THF the order Rb(5.70) > Li(5.73) > K(5.75) > Na(5.80) was taken to indicate contact ion pairs with Rb, K, and Na but the possibility of a small fraction of solvent-separated ion pairs with Li. Applying this idea to cyclooctatetraenide complexes of the lanthanides, the chemical shifts in THF for $Y(C_8H_8)_2^-$ (δ5.75)[11] and $La(C_8H_8)_2^-$ (δ5.90)[11] would imply more solvent-separated ion pairs with yttrium.

Returning to the mixed sandwich complexes, we see that with the unsolvated compounds the resonance of the C_8H_8 ring has experienced a downfield shift from its position in the corresponding alkali metal and anionic bis(cyclooctatetraenide) complexes. This seems to be in accord with the simple polarization arguments expressed above and would indicate a smaller effective electron density on the C_8H_8 ring in the neutral mixed sandwich complexes. However, surprisingly, the resonance of the C_5H_5 ring has suffered an upfield shift, its position being at higher field than in alkali metal cyclopentadienides. Since it does not seem reasonable to assume higher effective charge on the C_5H_5 ring in the present complexes than in alkali metal derivatives, some other factors must be responsible for the upfield shift. Although by no means certain, a possible rationale could be the "ring current" effect of the C_8H_8 ring on the cyclopentadienide protons. The structure of the mixed sandwich complexes in solution could very well approach that of $(C_5H_5)Ti(C_8H_8)$[79] which is known to contain two planar and parallel carbocyclic rings. In such a structure the protons of the smaller five-membered ring are somewhat over the electron cloud of the larger eight-membered moiety, in the shielding region,[98] and might experience some upfield shift. Another puzzling observation comes from the ^1H NMR data of the adducts. Reference to Table 16 shows that dissolving the Lu and Y complexes in pyridine-d_5 or recording the spectrum of the isocyanide adduct in toluene-d_8 has resulted in a downfield shift of approximately 0.2 ppm for the cyclopentadienide ring protons whereas the resonance position of the C_8H_8 ring has remained constant. Based on the discussion in Chapter II concerning the involvement between the lanthanide ion and the carbocyclic rings in these complexes we might have anticipated greater changes in chemical shifts of the C_8H_8 protons than those of the C_5H_5 ring. However, we have already noted a large downfield shift in $Ca(C_5H_5)_2$ when dissolved in pyridine, a result which has no ready explanation. Also in the unsolvated mixed sandwich complexes it appears that more than one factor is controlling the observed chemical shifts. Thus it may not be surprising that the simple trend in chemical shifts upon adduct formation, that we expected (hoped for) is not actually observed.

We have no explanation for this NMR behavior.

The ^{1}H NMR spectra of the paramagnetic lanthanide complexes differed from the diamagnetic analogues in that the peaks due to the carbocyclic rings were broadened and their position shifted from the diamagnetic values. Both of these observations are typical of paramagnetic complexes. In the absence of structural information and temperature-dependent NMR studies it is impossible to comment upon the significance of the magnitude of these shifts.

iv) Electronic Spectra

The electronic spectra of the mixed sandwich complexes offer an additional probe for observing solution properties of these complexes. However, due to their low solubility in non-donor solvents it will only be possible to obtain data for the base adducts. Furthermore, we have only recorded the spectra at room temperature and the objective here is not to make quantitative but only qualitative comparison with the existing data on the "free" lanthanide 3+ ions and, where appropriate, with the corresponding organolanthanide derivatives.

Complexes of the lanthanides typically display rather sharp, weak electronic absorption spectra. These are attributed to f-f electronic transitions mainly occurring in the visible region and being responsible for the color of the ions.[2] Of course Y^{3+} and La^{3+} possessing no f-electrons and Lu^{3+} having a completed shell of f-electrons will not be capable of displaying such f-f transitions. As was discussed in the introduction, the general scheme is to compare the data for the f-f transitions to that of the respective aquo ion. The changes in line position and intensity, the splitting of the bands, and the positions of charge transfer bands give some idea of the ability of the ligands to perturb the electronic transitions of what is considered the relatively unperturbed f levels of the aquo ion.

In Figure 9 portions of the spectra are displayed for the neodymium, holmium, and erbium mixed sandwich complexes in tetrahydrofuran. As expected, there are a number of sharp, weak lines in the visible region of the absorption spectrum. There is also a strong band at the high energy side of each spectrum, and in the holmium complex it appears to be partly responsible for the broadness of the band at 432 nm. More complete spectra are collected in Table 17 for these complexes and the ytterbium analogues. The data in Table 17 are arranged in band groups which were obviously separated

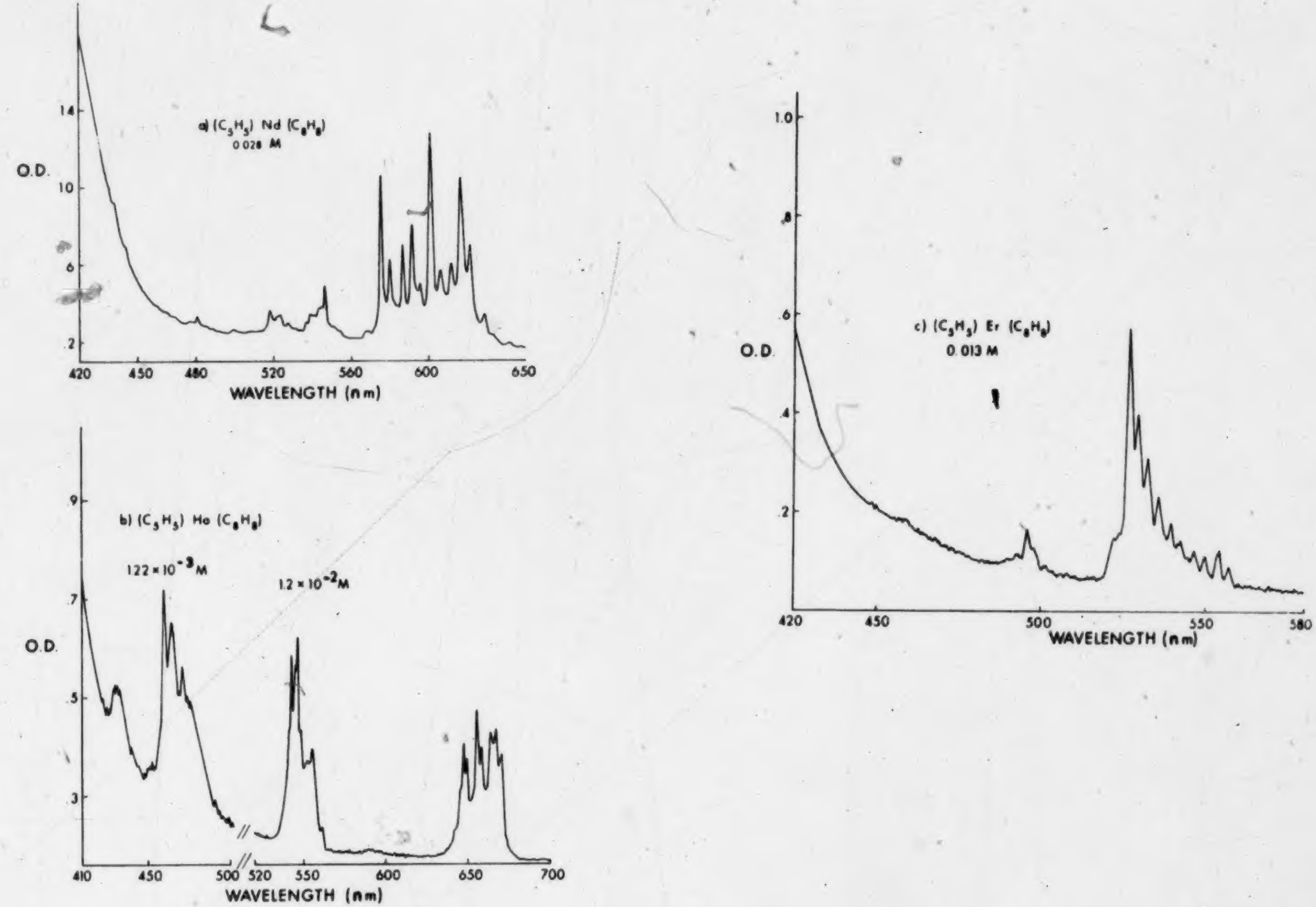


Figure 9. Electronic spectra of $(C_5H_5)M(C_8H_8)$ Complexes (M = Nd, Ho, Er) in THF.

Table 17. Electronic Spectra of $(C_5H_5)M(C_8H_8)$ Complexes in THF and Comparative Data for M^{3+} Aqueous Ions.[a,b]

Ho λ	Ho ε	Ho^{3+}(aq)	Assignment	Er λ	Er ε	Er^{3+}(aq)	Assignment	Yb^d λ	Yb^d ε	Yb^{3+}(aq)	Assignment
432	142			353	600			338	57		
453	117	450	$^5G_6$	417(sh)	62			375	54		
462	417			458	14	449	$^4F_{5/2}$	410	28		
466	350							580	163		
472	270			493	9	485	$^4F_{7/2}$	629(sh)	88		
478	199			496	13			654	72		
541	26	542	$^5F_4$, $^5S_2$	498(sh)	10			794	17		
543	44			501	7			806	6		
545	42			527	44	520	$^2H_{11/2}$	835	20		
547	50			529	31			897	12		
548	27			533	24			930	11	935-971	$^2F_{5/2}$
552	22			536	18			955	15		
561	8			539	14			974	25		
646	26	648	$^5F_5$	543	11	541	$^4S_{3/2}$	979	20		
650	22			547	10			990	27		
656	33			549	9			1055	27		
658	25			554	10			1195	29		
664	27			557	7						
668	29										
671	23										

continued....

Table 17 (continued)

Nd		Nd^{3+}(aq)		Nd		Nd^{3+}(aq)		Nd		Nd^{3+}(aq)	
λ	ε		Assignment	λ	ε		Assignment	λ	ε		Assignment
439	28			568	3	575	$^4G_{5/2}, ^2G_{7/2}$	741	2		
445(sh)	21			569	4			747	2	736	$^4F_{7/2}$
465	7	462	$^4G_{11/2}$	576	36			755	5		
471	6			580	18			763	1		
477	6			587	20			769	1		
479	6			592	24			786	1	792	$^4F_{5/2}$
481	7			596	13			793	2		
499	4			601	44			800	6		
508	4	509	$^4G_{9/2}$	606	16			803	7		
519	8			612	18						
522(sh)	6			617	32						
524	7			621	22	625^c	$^2H_{11/2}$				
528	5			629	8						
537	5	521	$^4G_{7/2}$	641	1						
539	7			675	1	674	$^4F_{9/2}$				
541	7			682	2						
543	8			687	1						
545	9			688	2						
547	13										

Footnotes for Table 17.

[a] Wavelength in nm, error in the molar extinction coefficient, ε, approximately 15%.

[b] Baricenter of the bands as reported in Ref. 99.

[c] Approximate value from graph in Ref. 100.

[d] No f-f transition in the visible region; aqueous data from Ref. 101.

from one another. The data for the aquo ion[99-101] with its assignment is then placed next to the band, or region of a more extended grouping, based on similarities in wavelengths. Only the baricenter of the band is reported for the aquo complexes. As this requires knowledge of the ground and excited state splittings, which is not available from these room temperature spectra of the mixed sandwich compounds, all the observable bands within the group are reported. No analysis of any possible vibrational structure or the splittings of the levels is possible without detailed spectral analysis.

First, looking at the neodymium, holmium, and erbium data it is evident that a general red shift occurs relative to the corresponding bands of the aquo ion. Similar, albeit smaller, red shifts are also observed when the comparison is extended to include the tricyclopentadienide derivatives. For instance, the spectrum of $Er(C_5H_5)_3$[62] shows absorptions for $^4S_{3/2}$ at 546-540 nm, for $^2H_{11/12}$ at 530-499 nm, and for $^4F_{7/2}$ at 494-484 nm; in the $Nd(C_5H_5)_3$[105] complex there are the bands, $^4F_{9/2}$ 689 (very weak)-671 nm, $^2H_{11/2}$ 629(very weak)-620 nm and $^4G_{5/2}$, $^2G_{7/2}$ 596-574 nm. These red shifts are a result of decreases in both the interelectron repulsion among f-electrons and spin-orbit coupling in the complexes,[12b] commonly known as the nephelauxetic effect. It is considered to represent a tendency toward more covalent bonding relative to the aquo ions.[106] The general conclusion, based on band position changes, that the nephelauxetic effect is more pronounced in the cyclopentadienide complexes than in the aquo ions is quite reliable since it follows from detailed studies of the $M(C_5H_5)_3$ compounds. However, a more cautious interpretation is warranted for the shifts presented above for the mixed sandwich complexes. As pointed out before, the splitting of the ground state and assignment of the excited state levels are necessary to exactly deduce the appropriate value of the shift. Although not available in the present complexes, the apparent conclusion that the nephelauxetic effect increases in the order "free ion" $< M(C_5H_5)_3 < (C_5H_5)M(C_8H_8)$ is at least in accord with chemical intuition and might even be proven by detailed spectroscopic studies on these compounds.

In addition to the band position, intensities are also of interest. Certain absorptions termed hypersensitive transitions exhibit considerably enhanced intensity as the ligand environment changes. Hypersensitivity has previously been interpreted both as an indication of the low point symmetry at the metal ion[107] and as some measure of covalency in the metal-ligand interaction.[108] It is not possible here to assess the mechanism of hypersensitivity, but the bands termed hypersensitive can be identified. For neodymium it is the $^4G_{5/2}$ level that contains the hypersensitive band, in holmium it is the $^5G_6$ level, and in erbium the $^2H_{11/2}$ level. It is then interesting that these are the same levels that contain the most intense bands assigned as f-f transitions in Table 17.

The ytterbium complex deserves a few comments of its own. For Yb^{3+} only one band is expected for the $^2F_{5/2} \leftarrow {}^2F_{7/2}$ transition. The spectrum appears to be more complex in the f-f region than the aquo ion and in addition displays two broad absorptions at ~360 nm and ~580 nm, the last band being responsible for the intensely blue color of the complex. The relatively high intensity and the broadness (width at half-height for the band at 580 nm is on the order of 100 nm) of these absorption bands indicate that they do not originate from f-f transitions. It is interesting to note that the $Yb(C_5H_5)_3$ complex was also unique among the tricyclopentadienide derivatives of the lanthanides in these regards. The colors and spectra of the tricyclopentadienide lanthanide complexes corresponds closely to the aquo ions in solution, with the exception of $Yb(C_5H_5)_3$. This intensely green compound displays a number of absorptions over the range 870-1053 nm, many of which are suggested to be vibronic in character, and exhibit two additional broad bands in the violet, 379 nm ($\varepsilon = 260$), and in the red, 649 nm

(ε = 9).[63a] For the absorption in the red region Fischer[30] has reported two bands at 610 (ε = 36) and at 649 nm (ε = 46) for a benzene solution of the THF adduct. The similarity between the spectra of the $(C_5H_5)Yb(C_8H_8)$ and $Yb(C_5H_5)_3$ complexes is clearly apparent. The origin of these broad absorptions is not totally clear. Calderazzo *et al.*[63b] suggested that they may be due to either 4f → 5d transitions or to charge transfer from ligand-to-metal. The fact that the bands are only observed in ytterbium which has a readily available 2+ oxidation state would seem to be more in line with the charge transfer mechanism. Broad intense bands have also been identified by Streitweiser *et al.*[11] in the $M(C_8H_8)_2^-$ complexes. The metal dependence of the band maxima led Streitweiser to postulate that these bands were ligand-to-metal charge transfer in character. The ligand dependence of the band positions is also in accord with the above suggestion. As noted above, with the exception of ytterbium, the tricyclopentadienide derivatives do not display broad bands in the visible region. Replacement of the $C_5H_5^-$ by the more easily oxidized (more reducing) $C_8H_8^{2-}$ ligand should move the ligand-to-metal charge transfer band to longer wavelength.[103] The broad bands in the visible region for the $M(C_8H_8)_2^-$ complexes reflect this expectation.

A similar shift on going from $Yb(C_5H_5)_3$ to (C_5H_5)-$Yb(C_8H_8)$ should be observed if the band around 600 nm is charge transfer in character. However, such a simple correlation may not be expected due to the apparently special circumstances which give rise to the bands in the visible region in $Yb(C_5H_5)_3$. In the study of this molecule, Jorgensen[63a] points out that the band at 649 nm is too low in energy considering the reducing power of the cyclopentadienide anion. Furthermore, should this band be a regular charge transfer transition, the corresponding absorption in $Eu(C_5H_5)_3$ should be observed at longer wavelength since Eu^{3+} is more oxidizing than Yb^{3+}. In fact the reverse is seen. Jorgensen feels that the unusually strong reducing character of the $C_5H_5^-$ ligand in $Yb(C_5H_5)_3$ is due to the small ionic radius of Yb^{3+} which causes ligand-ligand repulsion. The effect of this repulsion is to raise the energy of the M.O.'s obtained from the combination of cyclopentadienide π-orbitals, in particular the one having nodes between each C_5H_5 ring. Transfer of an electron from this high energy orbital to the metal is postulated to give rise to the band at 649 nm. It is also felt that the odd parity of this M.O. is responsible for the unusually low intensity of this band. Transition from the remaining ligand M.O.'s to the metal produces the high energy band at 380 nm. According to Jorgensen, ligand-ligand interaction in these M.O.'s is smaller and the band position is more representative for the reducing character of a single cyclopentadienide ligand. Consistent with the argument is the observation that replacement of the $C_5H_5^-$ ligand by chloride ion removes the band at 649 nm. Assuming Jorgensen's analysis to be correct the absence of broad bands below 649 nm in the spectrum of $(C_5H_5)Yb(C_8H_8)$ is not too surprising. Replacement of two $C_5H_5^-$ rings by the $C_8H_8^{2-}$ anion should result in the elimination of the latter band as observed in (C_5H_5)-$YbCl_2$ and $(C_5H_5)_2YbCl$. The appearance of a band at ~580 nm, some 200 nm displaced from the band position expected from a "regular" $C_5H_5^-$ ligand, could in fact be construed as displaying the characteristic red shift of a ligand-to-metal charge transfer band as the more reducing $C_8H_8^{2-}$ ligand is added to the complex. Of course the difficulty with this analysis is that it is impossible to estimate with the present data at hand how much of the shift is due to the more reducing nature of $C_8H_8^{2-}$ and how much to ligand-ligand repulsions similar to the ones outlined for $Yb(C_5H_5)_3$. In this regard a comparison between the Yb and Eu mixed sandwich complexes would appear to be useful. Since the importance of ligand-ligand interactions is apparently smaller in the Eu complex the shifting of this low energy band could conceivably give an indication of the relative reducing power of the $C_8H_8^{2-}$ ligand. It is also interesting to note that, consistent with the removal of the special nodal properties of the highest ligand M.O. present in $Yb(C_5H_5)_3$, the intensity of the low energy band in $(C_5H_5)Yb(C_8H_8)$ has increased significantly. This lends further support to the cyclooctatetraenide-to-metal charge transfer character of this band.

Concurrent with the changes in the low energy absorptions, the violet region of the spectrum has also undergone noticeable transformations, the exact extent being difficult to assess. The three bands at 338, 375, and 410 nm are less intense in the mixed sandwich complex than the band at 379 nm ($\varepsilon = 260$) in $Yb(C_5H_5)_3$. However, these bands are actually sitting on the tail end of a more intense absorption that originates in the ultraviolet. It is possible that the charge transfer band observed in $Yb(C_5H_5)_3$ at 379 nm is in fact in the near ultraviolet in the $(C_5H_5)Yb(C_8H_8)$ compound. Should this be the case, a plausible explanation would be that the presence of the $C_8H_8{}^{2-}$ anion has rendered the $C_5H_5{}^-$ ligand less reducing in the mixed sandwich complex than in the tricyclopentadienide derivative.

It also appears that the spectral features of the ytterbium mixed sandwich complex are dependent on the nature of the donor. Donor dependence of the band positions has been noted by Fischer[30] in $Yb(C_5H_5)_3 \cdot L$. He noticed that as the ligand is changed in the series $P(Ph)_3$, THF, py, CNC_6H_{11}, and NH_3 the low energy band underwent a blue shift, the band maxima being at 655, 650, 640, 611, and 608 nm, respectively. The color of a THF solution of the mixed sandwich complex is blue. However, a solution prepared from the cyclohexylisocyanide adduct in toluene is intensely green. The spectrum of the toluene solution is similar to the THF spectrum in the 880 to 1100 nm region but the 580 nm band is now absent and there are slightly broadened bands at 745 (shoulder, $\varepsilon = 35$) and 780 nm ($\varepsilon = 55$). There is also a shoulder at higher energy, 430 nm ($\varepsilon = 140$), which is flanked by a more intense band trailing into the ultraviolet. Unfortunately, the maxima of this last band could not be observed due to decomposition problems at the low concentration necessary to record the spectrum. The changes are obviously more complicated in this case than in the $Yb(C_5H_5)_3 \cdot L$ complexes, but we have no explanation for the changes.

It is clear that a more thorough investigation will have to be carried out before the intricacies of the electronic spectra for $(C_5H_5)Yb(C_8H_8)$ and its adduct can be fully accounted for. The data presented here and in previous sections illustrate that the combination of the reducing $C_8H_8{}^{2-}$ ligand and the availability of the 2+ oxidation state of the metal confer some unusual properties upon the mixed sandwich complexes of ytterbium.

Returning to the data in Table 17, it can be seen that some higher energy bands are observed in the Ho, Er, and Nd complexes. These bands are not assigned as f-f transitions as they are relatively broad absorptions, and they occur on the side of a strong charge transfer band which rises dramatically just beyond the highest energy bands noted in the table. Attempts to locate the λ_{max} of the strong high energy band were not fruitful due to difficulties in handling the necessarily dilute solutions of these very air sensitive compounds and the problem of the solvent beginning to absorb in the high energy region. The spectrum of dipotassium cyclooctatetraenide itself displays a very strong $\pi^* \leftarrow \pi$ charge transfer band well in the ultraviolet with λ_{max} below 250 nm.[102] Since the charge transfer band for the mixed sandwich complexes extends well into the visible region it is clear that it is not of the same origin as the $\pi^* \leftarrow \pi$ transition in the cyclooctatetetraenide dianion. As noted before, absorption in the visible region were observed by Streitweiser *et al.*[11] for the $M(C_8H_8)_2^-$ complexes and the bands were assigned as ligand-to-metal charge transfer. Inspection of the near ultraviolet and visible region of spectra available for the tricyclopentadienide lanthanide derivatives do not appear to display such absorptions. Based on these observations, we would like to suggest that the band tailing into the visible region in the spectra of the mixed sandwich complexes is ligand-to-metal charge transfer in character. This would be in keeping with the expected effect on the band position with the change in reducing character of the ligands around the central metal.[103,104,46]

It is thus apparent from the electronic spectra that the mixed sandwich complexes occupy a position intermediate between the neutral tricyclopentadienide complexes and the anionic bis(cyclooctatetetraenide) lanthanide derivatives.

v) Reactivity of the Complexes

Before proceeding with discussion of the reactivity of the ligands within the mixed sandwich complexes a general comment about the range of base adducts is in order.

It is well known that lanthanide ions favor interaction with oxygen donors and to a lesser extent with nitrogen ligands.[6,109] This seems to be borne out by the types of base adducts so far isolated for organolanthanides here and in previous studies.[15b,30,33,34] As mentioned already, the displacement of coordinated THF from the mixed sandwich complexes by isocyanide and the ability of the tricylcopentadienide derivatives to form stable adducts with phosphines and thioethers indicate a change toward softer Lewis acidic character of the lanthanide ion in these organometallic complexes.

In this study, not all the nitrogen ligands used permitted isolation of an adduct. Attempts to prepare the 2,3-dichloropyridine adduct of the erbium mixed sandwich complex *via* eq. (III-2) produced a color change from light pink to orange-yellow as the complex dissolved in toluene, but the adduct could not be isolated from the clear solution. Reaction of triethylamine with the holmium complex likewise resulted in a clear yellow solution from which only the parent mixed sandwich complex could be obtained. A similar problem was encountered with $P(n\text{-}Bu)_3$. The holmium complex again dissolved in toluene and the yellow color of the complex lightened but no adduct could be isolated. The inability to isolate adducts with these bases could reflect the inherently weaker Lewis acid strength of the $(C_5H_5)M(C_8H_8)$ compounds compared to the $M(C_5H_5)_3$ derivatives. It also could be related to the more insoluble nature of the base free compounds which could precipitate in preference to the adduct upon addition of hexane to the toluene solution.

The compounds react very readily with oxygen and water. They oxidize violently upon exposure to air and often inflame spontaneously. The products of hydrolysis have been identified by mass spectrometry and NMR spectroscopy as cyclooctatrienes and cyclopentadiene.

In a less violent reaction, which demonstrates that the cyclooctatetetraenide moiety retains its reducing power, mercury(II)chloride was added to a tetrahydrofuran solution of $(C_5H_5)Ho(C_8H_8)$ at room temperature. This first led to a clear light yellow solution which after five minutes began to deposit mercury metal. Previously dilithium cyclooctatetrenide was reacted with chlorides of zinc, cadmium, and copper(I) producing the respective metal and cyclooctatetraene.[110]

The lability and transferability of the carbocyclic rings in organolanthanide complexes containing the individual ligands have been noticed before. Thus, it was not surprising that the reaction between the yttrium mixed sandwich complex and UCl_4 occurred readily at 0°C to produce uranocene. As the UCl_4 was added to the yellow solution of the yttrium complex a green-brown color was immediately obtained. Uranocene was characterized by its visible spectrum and by its mass and ^1H NMR spectrum after sublimation.[35b] Similarly the reaction of the holmium complex with FeI_2 proceeded rapidly at room temperature. Removal of the solvent followed by sublimation produced the expected orange ferrocene which was identified by its ^1H NMR and mass spectrum.

To gain a measure of the relative reactivity of the cyclic ligands in the complexes, the reaction of $(C_5H_5)Y(C_8H_8)$ with trimethylchlorosilane was carried out. As shown in Figure 10 the main reaction corresponds to the following:

$$(C_5H_5)Y(C_8H_8) + 2Me_3SiCl \xrightarrow[R.T.]{py\text{-}d_5} C_8H_8(SiMe_3)_2 + C_5H_5YCl_2 \qquad \text{(III-4)}$$

The reaction was carried out in an NMR tube by incremental addition of trimethylchlorosilane. In Figure 10a the resonances for the complex before reaction are displayed and marked with X throughout the figure. After addition of approximately 29 mole %, according to the stoichiometry of Eq (III-4), of trimethylchlorosilane, the spectrum shown in Figure 10b is obtained. The new resonance at δ6.5 and 0.2 are assigned to $(C_5H_5)YCl_2$, and to the $SiMe_3$ protons, respectively. As more Me_3SiCl is added, Figure 10c, the resonances of the starting material decrease while those of $(C_5H_5)YCl_2$ and $-SiMe_3$ groups increase in intensity. Having added a 10% excess of the silicon reagent, Figure 10d results. It is seen that all of the starting complex has been consumed and a new signal at δ0.4 for the unreacted Me_3SiCl appears (note in Figure 10d the spectral amplitude at which the high field part of the spectrum was recorded, is reduced to keep the signal on scale). Finally, as more Me_3SiCl is added, Figure 10e, no apparent reaction occurs. However, when the solution is allowed to stand overnight, at room temperature, the spectrum in Figure 10f results, which shows that the intensity of the C_5H_5 resonance

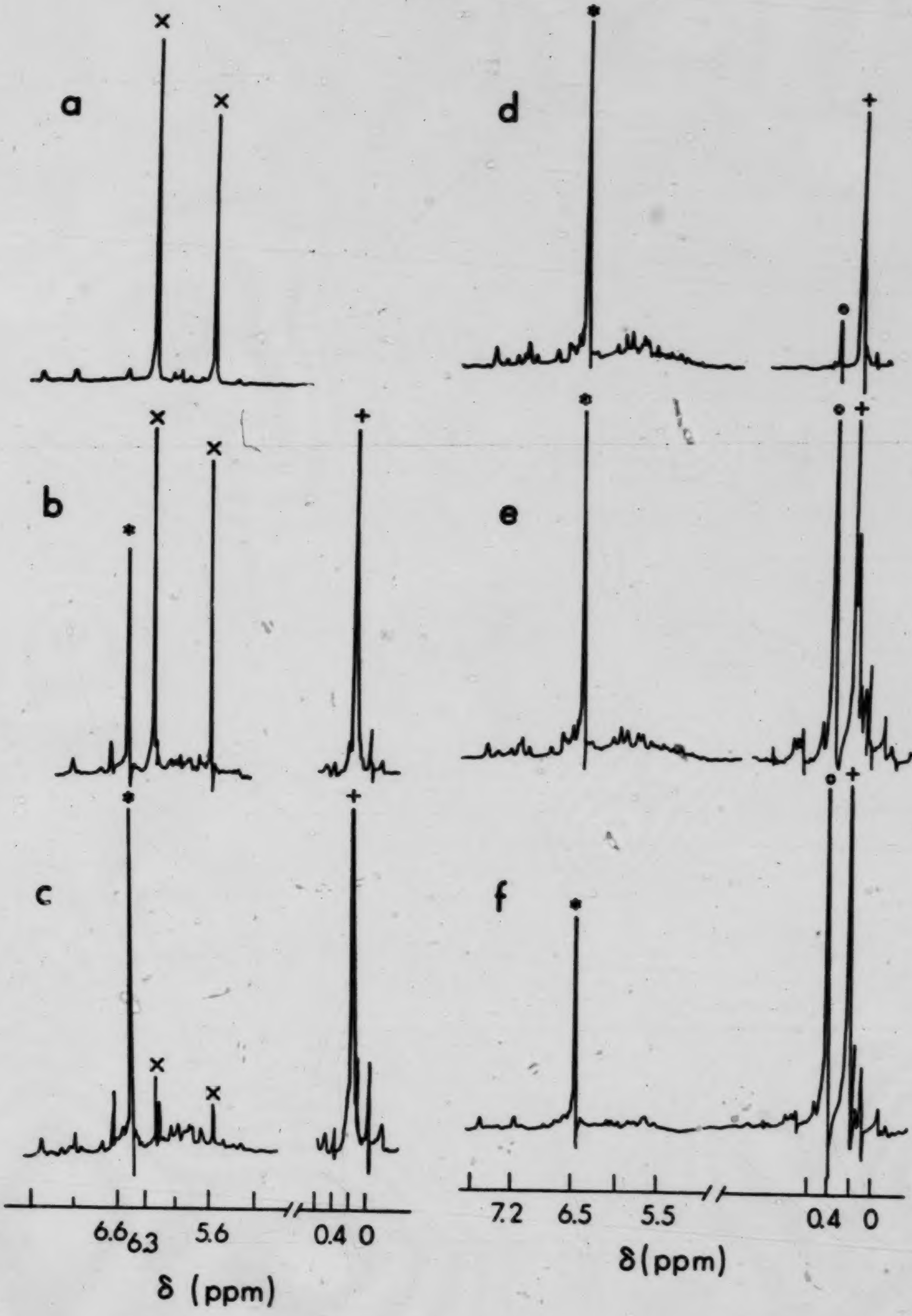
Figure 10: Reaction of $(C_5H_5)Y(C_8H_8)$ with incremental addition of Me_3SiCl followed by NMR.

x = Original C_5H_5, C_8H_8 resonances.

* = Resonance assigned to $(C_5H_5)YCl_2$.

+ = Resonance due to $-SiMe_3$ groups in $C_8H_8(SiMe_3)_2$.

o = Excess Me_3SiCl.


a
b
c
d
e
f
×
*
+
6.6
6.3
5.6
0.4
0
δ (ppm)
7.2
6.5
5.5
0.4
0
δ(ppm)

also begins to decrease. The data clearly show the cyclooctatetetraenide moiety reacting very much faster than the cyclopentadienide ring. That the organic product is the same as that obtained in the reaction of dipotassium cyclooctatetetraenide with trimethylchlorosilane is not immediately obvious. The product of the reaction was identified by Andrews and Rakita[111] as 5,8-bis(trimethylsilyl)-1,3,6-cyclooctriene which exhibited resonances in $CDCl_3$ at δ-0.02 (singlet), 2.7-2.9 (multiplet), 5.3-5.9 (multiplet) in the ratio 15.7:2.0:6.1. In Figure 10 with pyridine-d_5 as solvent, the singlet for the $-SiMe_3$ groups appears at 0.2 ppm and the low field multiplet (δ5.5-6.2) is at slightly lower field than reported in the literature. To eliminate the apparent solvent effect on the chemical shifts the reaction was repeated with the erbium mixed sandwich complex followed by isolation of the organic product. A portion of the spectrum obtained in $CDCl_3$ is shown in Figure 11. The spectrum agrees well with the literature data. Additionally, a mass spectrum of the compound displays prominent peaks identical to those reported by Andrews and Rakita.[111] Hence the products obtained from $K_2C_8H_8$ and $(C_5H_5)M(C_8H_8)$ complexes are identical.

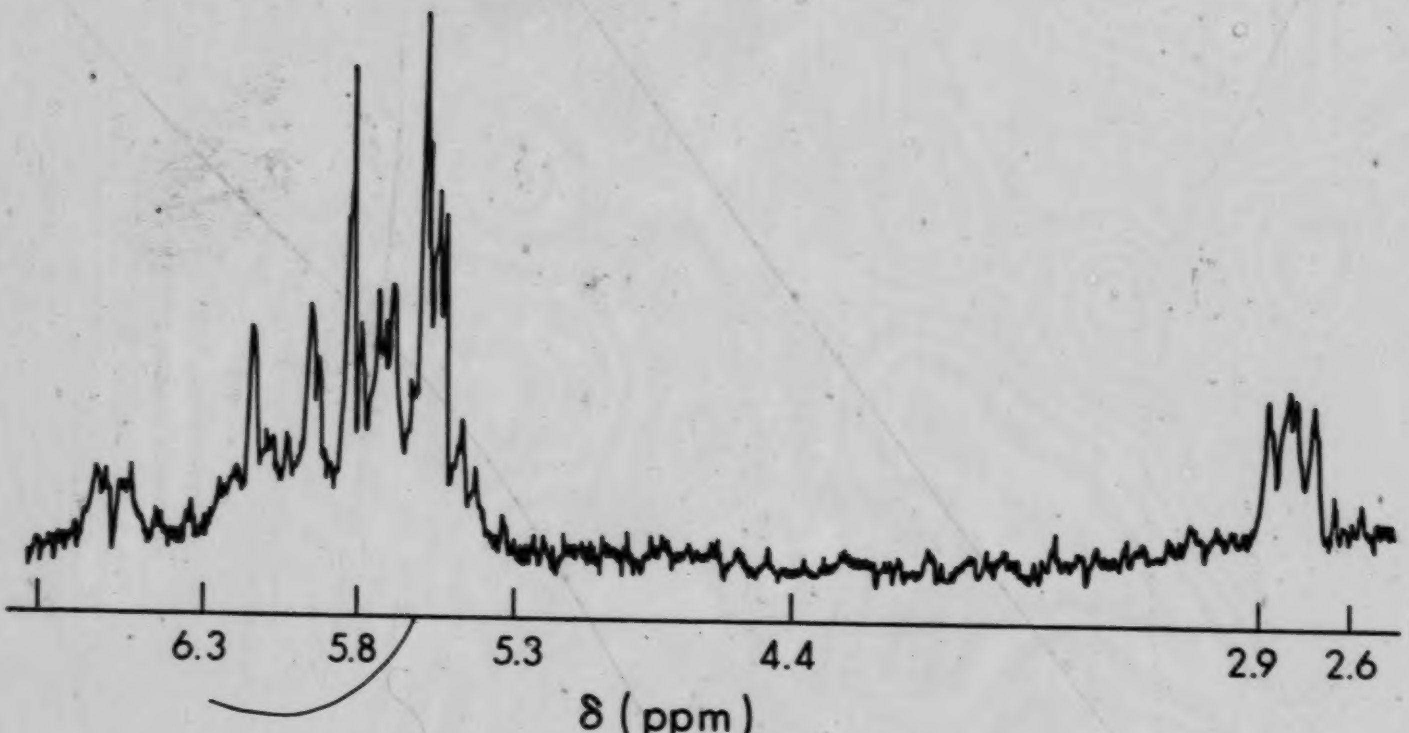


Figure 11: Detail of the ^{1}H NMR spectrum of $C_8H_8(SiMe_3)_2$ obtained by reaction of $(C_5H_5)Er(C_8H_8)$ with Me_3SiCl.

4. Conclusion

The isolation of a number of base adducts establishes the Lewis acidic character of the lanthanide mixed sandwich complexes. However, compared to the tricyclopentadienide derivatives the present complexes exhibit weaker Lewis acid behavior and this is attributed to the presence of the more reducing cyclooctatetetraenide moiety.

The pentahapto and octahapto bonding of the carbocyclic ligands in the base adducts is retained as suggested by infrared and nuclear magnetic resonance data. The molecular structure of the adducts is most probably comprised of two planar carbocyclic rings inclined to some degree with respect to one another and the base occupying a coordination position in the plane bisecting the metal-ring centroid vectors.

The spectral results and chemical properties of the adducts indicate that, as was the case with (C_5H_5)-$M(C_8H_8)$, $M(C_5H_5)_3$ and $M(C_8H_8)_2^-$ complexes, the bonding in the base adducts is also highly ionic in character. On a more subtle level, it was argued, based on infrared data, that the involvement of the more polarizable cyclooctatetetraenide ring with the metal is more important than that of the five-membered ring. The infrared and mass spectral data also seem to be consistent with the notion, already observed in the base free complexes, that the electrostatic component of the bonding is slightly greater while the overall strength of the interaction is weaker between the lighter lanthanide ions and the carbocyclic rings than with the heavier and smaller members of the series. The presence of the more reducing cyclooctatetetraenide ring also manifests itself in the electronic spectra of the complexes. Although the f-f transitions are only mildly perturbed by the ligand field, the nephelauxetic effect appears to be greater in $(C_5H_5)M(C_8H_8)\cdot L$ complexes than in analogous $(C_5H_5)_3M\cdot L$ compounds. Absorptions in the visible region which could be assigned as ligand-to-metal charge transfer bands are not as prevalent as in $M(C_8H_8)_2^-$ compounds, of the complexes thus far investigated, only $(C_5H_5)Yb(C_8H_8)\cdot L$ displays such bands. Nevertheless, the observation of strong absorptions originating in the ultraviolet and tailing into the visible region, whereas the tricyclopentadienide complexes have no absorptions in this area, shows the effect of the cyclooctatetetraenide ligand. The shift is also in accord with the suggested charge transfer character of these bands.

The charge transfer character of some electronic absorptions and the presence of metal-ligand skeletal vibrations in the Raman spectra of the complexes denote some covalent interaction between the lanthanide metal and the ligands. This interaction, according to current views, is more probably due to orbital mixing between metal-d and ligand π M.O.'s than the corresponding overlap with the 4f orbitals of the lanthanides.

However, it is also apparent that this contribution to the bonding has no real chemical significance. The reactivity of the complexes is typical of the ionic salts and of the lanthanide complexes of the individual ligands. The compounds are extremely air and moisture sensitive and react rapidly with electrophilic reagents. The latter type of reaction with Me_3SiCl showed, not unexpectedly, that the $C_8H_8^{2-}$ ring is more reactive than the $C_5H_5^-$ ligand in these complexes. There is also very facile ligand exchange reaction and the interaction with FeI_2 and UCl_4 produces the thermodynamically more stable ferrocene and uranocene, respectively.

Although providing the missing link between the neutral $M(C_5H_5)_3$ and ionic $M(C_8H_8)_2^-$ complexes, the present compounds provide yet another manifestation of the contrasting behavior between actinide and lanthanide organometallic derivatives; significant metal-ligand covalent interaction in the former and highly electrostatic bonding in the latter complexes.

CHAPTER FOUR

SYNTHESIS OF $Yb_2(C_8H_8)_3$: RELEVANCE TO PROBLEMS IN THE PREPARATION OF $(C_5H_5)M(C_8H_8)$.

1. Introduction

Lanthanide complexes with the stoichiometry $M_2(C_8H_8)_3$ have been isolated and characterized by DeKock *et al.*[14] and by Greco *et al.*[41] The work by the latter group involved reduction of a cerium(IV)alkoxide by triethylaluminum in the presence of cyclooctatetraene producing $Ce_2(C_8H_8)_3$ as described in Chapter I. The structure of this cerium compound is unknown. The preparation by Dekock *et al.* employed the metal atom synthesis technique and the structure of the neodymium complex was solved by X-ray diffraction.

The structure of the green neodymium complex isolated as the tetrahydrofuran adduct $Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$, is described as consisting of an ion pair having a $[Nd(C_8H_8)_2]^-$ anion and a $[Nd(C_8H_8)(C_4H_8O)_2]^+$ cation. The cation is observed to augment its coordination number by asymmetric coordination of three carbons from one of the C_8H_8 rings in the anion. This type of expansion of coordination is similar to that previously described for neodymium tris(methylcyclopentadienide).[78] Also, the average C-C bond lengths within the C_8H_8 rings are all equal within experimental error.

Our interest in complexes of this type arose from difficulties experienced in the synthesis of the mixed sandwich complexes. As briefly indicated in Chapters II and III the yields of these complexes were never very good, the lighter lanthanides consistently giving the lowest obtainable amounts. Also with the lighter lanthanides a by-product in the reactions was identified, by mass spectrometry, as the tricyclopentadienide complex. This, at the time, was believed to be the sole by-product of the synthesis. Although, in some of the reactions the potassium or sodium chloride collected by filtration of the crude reaction mixture, was colored, air sensitive, and was obtained in amounts larger than expected from the quantities of starting materials utlilized. We thought the reason for this was coprecipitation of some of the desired mixed sandwich complex with the alkali halide. However on a large scale preparation of $(C_5H_5)Yb(C_8H_8)$, after removal of potassium chloride, there was obtained a small amount of material, less soluble than the mixed sandwich complex and clearly different from this last compound and also from $Yb(C_5H_5)_3$. This observation was contemporary to the original communication of DeKock on $M_2(C_8H_8)_3$ complexes.[14,113] The similar infrared spectrum of the by-product to DeKock's compounds led us to postulate that it was $Yb_2(C_8H_8)_3$. This complex of ytterbium was not isolated *via* the metal evaporation route, which gave cyclooctatetraenideytterbium(II) instead. This is not an unexpected result based on the well known ability of ytterbium to exhibit the 2+ oxidation state. In order to secure more firmly the nature of the by-product obtained in the $(C_5H_5)Yb(C_8H_8)$ synthesis, it became desirable to prepare the dinuclear compound by a more rational synthesis.

Having obtained evidence for another compound beside $M(C_5H_5)_3$ in the synthesis of mixed sandwich complexes, it of course became possible that the "extra alkali metal halides" in previous preparations were also $M_2(C_8H_8)_3$ type compounds. The general occurence of this type of compound and the relevance of $M(C_5H_5)_3$ and $M_2(C_8H_8)_3$ by-products to the problems associated with the synthesis of the mixed sandwich complexes will also be discussed in this chapter.

2. Preparation

The synthesis of $Yb_2(C_8H_8)_3$ could easily be accomplished by simply mixing the stoichiometrically required reagents, Eq (IV-1).

$$2YbCl_3 + 3K_2COT \xrightarrow[-60°C]{THF} Yb_2(C_8H_8)_3 + 6KCl \qquad (IV\text{-}1)$$

Reaction readily occured at -60°C immediately producing a deep blue solution upon addition of the dianion. The contents of the flask were maintained at -60°C for four hours and then allowed to warm slowly to room temperature.

No color change occurred during this time. The solution was then filtered to remove precipitated KCl which also contains some of the desired product and then cooling the filtrate to -20°C readily produces deep blue $Yb_2(C_8H_8)_3$. The compound is characterized by its identity to the by-product $Yb_2(C_8H_8)_3$ for which there is complete elemental analysis and by the similarity of its infrared spectrum to those reported by DeKock *et al.*[14] Also, qualitative tests for chloride and potassium ions were negative. Attempts to prepare crystals sutiable for X-ray investigation are still in progress.

3. Results and Discussion

The direct reaction of cyclooctatetraene dianion with anhydrous ytterbium(III)chloride provides a convenient route to the synthesis of the very air sensitive $Yb_2(C_8H_8)_3$. The deep blue complex is not sufficiently volatile to obtain a mass spectrum, but attemtps at running the mass spectrum indicate that tetrahydrofuran is absent in the complex as does the analytical and infrared data. This is in contrast to the analogous compounds preprared by DeKock which crystallize from THF with two coordinated solvent molecules. It will be instructive to compare the properties of this complex with those of $Yb(C_8H_8)$ as the divalent, diamagnetic compound was the product obtained *via* the metal atom synthesis technique and might also have been the expected by-product in the $(C_5H_5)Yb(C_8H_8)$ synthesis.

Employing the method of Hayes and Thomas[39] $Yb(C_8H_8)$ was prepared by reaction of ytterbium metal with cyclooctatetraene in liquid ammonia. This produced, after removal of coordinated ammonia, a red complex which was extremely air sensitive and difficult to handle. Its solubility in tetrahydrofuran is even lower than that of $Yb_2(C_8H_8)_3$. The synthesis however is not without difficulty. Attempts to obtain the ^1H NMR spectrum of the complex were frustrated by the presence of paramagnetic impurities. However, after taking the compound up in pyridine and forcing a small amount out of solution by the addition of hexane, it was possible to obtain a maroon product, most likely the pyridine adduct, which upon heating *in vacuo* at 110°C resulted in the red complex noted above. This compound gave satisfactory elemental analysis for $Yb(C_8H_8)$. The NMR spectrum of this apparently pure $Yb(C_8H_8)$ however still showed the presence of some paramagnetic component, possibly $(C_8H_8)YbNH_2$. Nevertheless its infrared spectrum was identical with the literature values. The infrared spectra of the red $Yb(C_8H_8)$ and the blue $Yb_2(C_8H_8)_3$ are compared in Figure 12. Table 18 lists these band positions and those of some related compounds. The infrared data clearly show a difference, as do the colors in the solid state, between the $Yb(C_8H_8)$ and $Yb_2(C_8H_8)_3$ complexes. Furthermore a

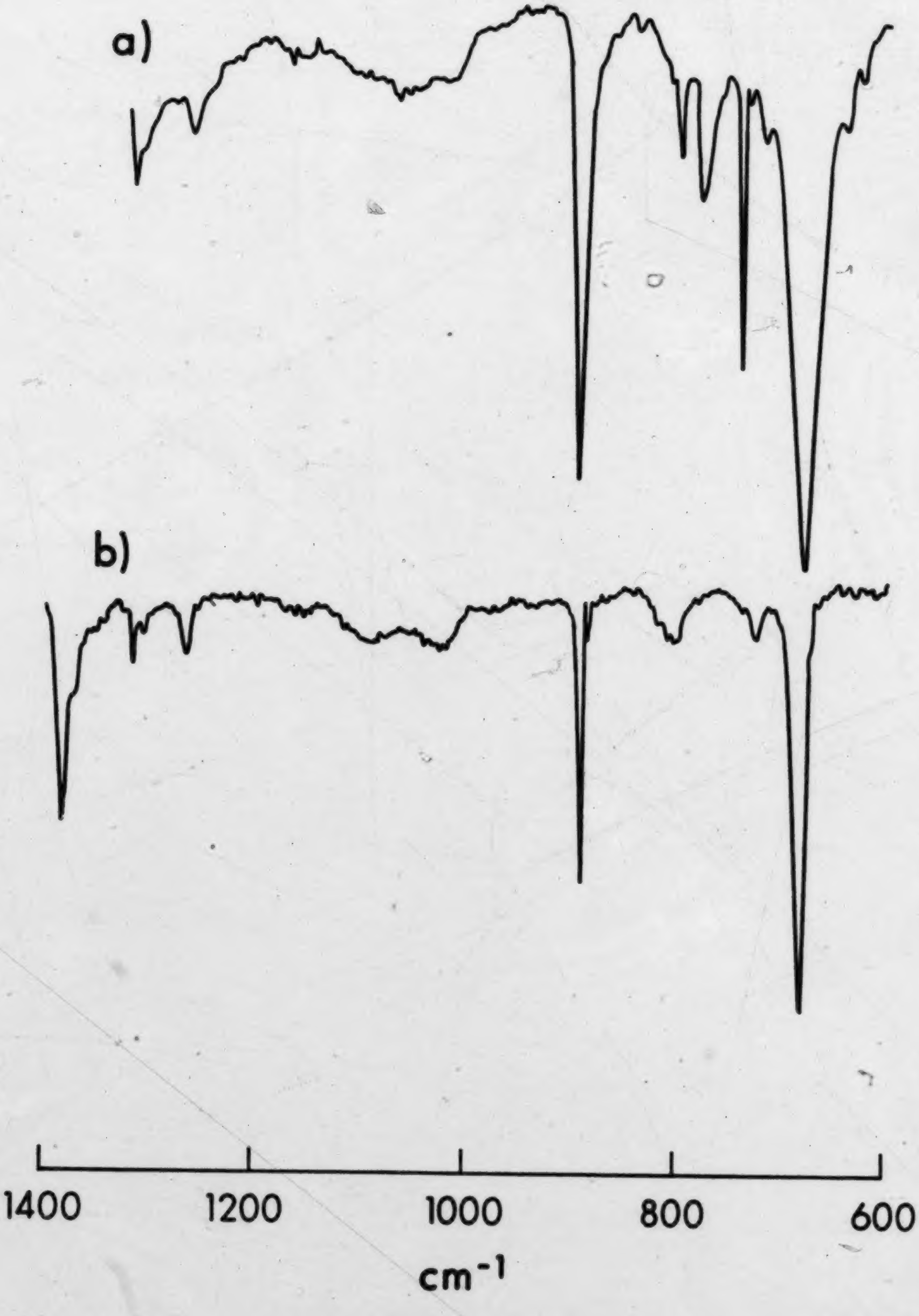


Figure 12: Comparison of the infrared spectrum of a) $Yb_2(C_8H_8)_3$ and of b) $Yb(C_8H_8)$.

Table 18. Infrared Data for $Yb_2(C_8H_8)_3$ and Related Compounds.[a]

$K_2C_8H_8$[b]	$Yb(C_8H_8)$[b,d]	$Yb_2(C_8H_8)_3$	$Nd_2(C_8H_8)_3$[b]	$KNd(C_8H_8)_2$[c]	$Lu_2(C_8H_8)_3$	$La_2(C_8H_8)_3$
880s	888s	894s	894s	890s	894s	891s
				810s		
		799m-w	798m	795s	797w	800w-m
		780m	771m	770m	782m	775vw
		740m-s	744s	730m	742s	740s
		695w		715m		
684s	678s	678vs	685vs	670vs	682vs	675vs
		668w			673w,sh	668w,sh

---

[a] Frequencies in cm^{-1}; vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

[b] Data from Ref. 14 and references therein.

[c] Data from Ref. 11.

[d] This work.

sample of Yb(C_8H_8) prepared by the metal atom synthesis technique, was kindly supplied by Professor DeKock. The color of this sample was also the same red as our compound, its ^{1}H NMR spectrum in pyridine-d_5 exhibited a sharp singlet at δ6.59 ppm in the expected region for a diamagnetic cyclooctatetraenide derivative. On the other hand attempts to record the NMR spectrum of the blue $Yb_2(C_8H_8)_3$ complex were met with failure, something we have consistently experienced with many of the paramagnetic organolanthanide derivatives. Also the color of a pyridine solution of the Yb(C_8H_8) complex is dark green-black whereas that of $Yb_2(C_8H_8)_3$ is deep royal blue.

Having shown that $Yb_2(C_8H_8)_3$ can be prepared it was an easy task to show that its properties were identical to the material obtained as the by-product in the preparation of the mixed sandwich compound. We next turned to the identification of complexes of the composition $M_2(C_8H_8)_3$ in the synthesis of mixed sandwich complexes for metals other than ytterbium.

Initially the lutetium reaction to produce the mixed sandwich complex was examined in more detail. The reaction was carried out in the usual manner. After removal of precipitated potassium chloride (which might also contain some $Lu_2(C_8H_8)_3$) followed by addition of hexane, a small amount of yellow solid was obtained readily. Washing with cold tetrahydrofuran produced a compound for which the elemental analysis indicated the stoichiometry $Lu_2(C_8H_8)_3$. The infrared spectrum, Table 20, was very similar to that for the related ytterbium complex. The ^1H NMR spectrum in pyridine-d_5 however exhibited only a singlet at δ6.40 ppm, whereas even for a symmetrical triple-decker-sandwich complex one would expect two singlets in a two-to-one ratio. A sharp singlet at room temperature was also observed for the $[Ti_2(C_8H_8)_3]^{2-}$ complex for which Skell *et al.*[112] have suggested a symmetrical structure and assumed accidental chemical shift equivalence of the two different ring systems for the observed singlet. In an attempt to resolve the ambiguity in the lutetium complex, the spectrum was recorded at -40°C. The sharp singlet persisted but its chemical shift now appeared at δ6.53 ppm. In addition a molecular weight determination in pyridine gave a value of 308 as opposed to 662, the expected value for the dinuclear unit. The temperature dependent chemical shift and the low value of the molecular weight both suggest a rapid equilibrium of the type shown in eq. (IV-2) in donor solvents.

$$Lu_2(C_8H_8)_3 \overset{L}{\rightleftharpoons} [Lu(C_8H_8)_2]^- + [Lu(C_8H_8)\cdot nL]^+ \qquad \text{(IV-2)}$$

This is not unreasonable in light of the crystal structure of the neodymium complex which indicates an ion pair in the solid state. Unfortunately the low solubility of the complex has prevented an NMR study in non-donor solvents.

Returning to the early lanthanides, the preparation of the mixed sandwich complexes for lanthanum and samarium were re-examined for the presence of the respective $M_2(C_8H_8)_3$ complexes. As noted in Chapters II and III it was very difficult to purify the mixed sandwich complexes for these elements. Again looking at the infrared spectrum of the complex that can be very readily forced out of the tetrahydrofuran reaction mixture, the characteristic features of Figure 12a are seen. These complexes were dried at room temperature *in vacuo* overnight so as to remove coordinated tetrahydrofuran. Note that with these early lanthanide complexes coordination of THF is also a feature of complex formation. This observation parallels DeKock's on $M_2(C_8H_8)_3(THF)_2$ complexes, which with the exception of erbium, are also early lanthanide derivatives. The infrared data, Table 18, for the lanthanum complex differs slightly from that reported by DeKock *et al.*[14] for the THF adduct, but it does closely agree with the spectrum of the analogous neodymium complex with the solvent removed. The lanthanum complex again gives a singlet in its NMR spectrum which occurs at δ6.65 ppm in pyridine-d_5. For comparison the spectrum of $K[La(C_8H_8)_2]$ gives a singlet at δ5.90 ppm in tetrahydrofuran. Both samarium and lanthanum complexes also give negative qualitative tests for chloride and potassium ions. These data and their comparison to the spectral properties of the ytterbium and lutetium dinuclear complexes suggests a similar formulation, $M_2(C_8H_8)_3$, for the samarium and lanthanum compounds. Although the syntheses of other mixed sandwich complexes were not re-investigated, the fact that $M_2(C_8H_8)_3$ was observed as a by-product with both early and late lanthanide metals lends support to the postulate that it was produced in the remaining preparations as well. The fact that the samarium and lanthanum complexes appeared to contain coordinated THF (as judged from mass spectral attempts) whereas the ytterbium and lutetium compounds were THF free, might suggest a greater solubility of the early lanthanide complexes in THF. This would lead to greater difficulties in separating the $M_2(C_8H_8)_3$ complex from the desired mixed sandwich species. This could partly explain the observation that the yields for the early lanthanide $(C_5H_5)M(C_8H_8)$ complexes were consistently lower than for the later lanthanide elements.

There is as yet no concrete evidence as to exactly how these dinuclear species are formed during preparation of the mixed sandwich complexes. However, for the early lanthanides it was noted that the tricyclopentadienide species were also produced and had to be separated from the mixed sandwich complexes by repeated crystallization.

The presence of both $M(C_5H_5)_3$ and $M_2(C_8H_8)_3$ in these preparations would suggest disproportionation of the mixed sandwich complex as a possibility for the formation of the by-products, eq. (IV-3).

$$3(C_5H_5)M(C_8H_8) \longrightarrow M(C_5H_5)_3 + M_2(C_8H_8)_3 \qquad \text{(IV-3)}$$

Equilibrium of this type is common to lanthanide complexes and has in fact been used advantageously in the synthesis of organolanthanide complexes, eq. (IV-4),[11] eq. (IV-5)[16] and eq. (IV-6).[17]

$$K[Ce(C_8H_8)_2] + CeCl_3 \xrightarrow{THF} [(C_8H_8)CeCl(THF)_2]_2 + KCl \qquad \text{(IV-4)}$$

$$2M(C_5H_5)_3 + MCl_3 \xrightarrow{THF} 3(C_5H_5)_2MCl \qquad \text{(IV-5)}$$

M = Sm, Gd, Dy, Ho, Er, Yb

$$Er(C_5H_5)_3 + 2ErCl_3 \xrightarrow{THF} 3(C_5H_5)ErCl_2 \cdot 3THF \qquad \text{(IV-6)}$$

Although a plausible reaction, the disproportionation is apparently not a feature of the chemistry of the heavier lanthanide $(C_5H_5)M(C_8H_8)$ complexes. Indeed, no $Yb(C_5H_5)_3$ could be detected by mass spectrometry in the preparation of the mixed sandwich complex, neither in the initially formed $Yb_2(C_8H_8)_3$ nor in the filtrate. In this particular case, and with other heavy lanthanides the formation of the dinuclear complex could involve displacement of the $C_5H_5^-$ moiety by the more basic $C_8H_8^{2-}$ ligand system and thereby represent a competition between the preparation of the mixed sandwich complex and the respective $M_2(C_8H_8)_3$. If this were the case, the control of stoichiometry becomes even more important in these reactions. We also note that the possibility of disproportionation reaction effecting the early lanthanide mixed sandwich derivatives would be another factor contributing to the reduced yields observed with these metals.

4. Conclusion

It has been shown that $Yb_2(C_8H_8)_3$ can be synthesized by conventional metathetical reaction between anhydrous $YbCl_3$ and the dianion of cyclooctatetraene as opposed to the metal atom vaporization technique. Furthermore complexes of similar stoichiometry have been suggested as one of the by-products in the preparation of the mixed sandwich complexes of the lanthanides and yttrium. Another by-product, $M(C_5H_5)_3$, has been observed only in the synthesis of the early lanthanide derivatives. The identification of these by-products shed some light on the difficulties encountered in the preparation of the mixed sandwich complexes. The differences seen in by-product formation show again that the chemical behavior of these early lanthanides is somewhat different from that of the heavier members of the series.

Part II

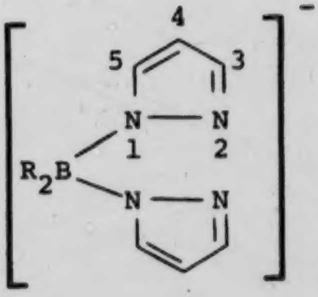
CHAPTER FIVE

SYNTHESIS AND PROPERTIES OF LANTHANIDE POLY(PYRAZOL-1-YL)BORATE COMPLEXES

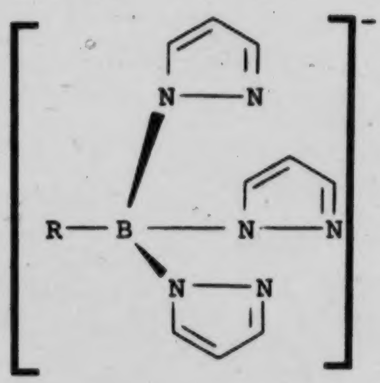
1. Introduction

In 1966 Trofimenko[114] introduced the poly(pyrazol-1-yl)borate ligand system, $[R_nBpz_{4-n}]^-$ (R = H, alkyl, aryl; n = 0, 1, 2; pz = 1-pyrazolyl moiety), to transition metal chemistry. It was hoped that this new ligand system would provide an extensive series of transition metal derivatives and, by virtue of its unique coordinating capabilities, eventually "...lead to a new subarea of coordination and organometallic chemistry."[115] This promise has been fulfilled to a large extent and progress in the field is summarized in two recent reviews.[116,117]

The initial work with the poly(pyrazol-1-yl)borate anions centered on the preparation and structural characterization of complexes mainly with the later transition metals.[115-117] The bis(pyrazol-1-yl)borate ions, (I), are uninegative four-electron donors formally analogous to β-diketonate ions and, not surprisingly, form neutral, monomeric bis chelate complexes, $M[R_2Bpz_2]_2$, with most divalent first-row transition metal ions.[118] Likewise, the tris- and tetrakis(pyrazol-1-yl)borate ions, (II), readily produce bis chelate complexes with divalent transition metal ions. Although capable of functioning as a bidentate chelate,[119,120] these ligands can and most often do exhibit a tridentate chelating bonding mode. In this configuration the ligands can be likened to the cyclopentadienide anion in the sense that both systems are uninegative, six-electron donors and occupy



(I)



(II)

three coordination sites on the metal. Of course the analogy is not a rigorous one since the cyclopentadienide anion forms π- rather than σ-bonded derivatives. Nevertheless, in an effort to compare the derivative chemistry of the two ligand systems a large number of transition metal complexes containing especially the tris(pyrazol-1-yl)borate moiety, ($HBpz_3$), instead of the cyclopentadienide anion have been synthesized: for example $[(HBpz_3)M(CO)_3]^-$ and $(HBpz_3)M(NO)_2Cl$ (M = Cr, Mo, W)[121] or $(Bpz_4)Mn(CO)_{3-n}L_n$ ($L = P(OR)_3$, n = 1, 2; $L = PR_3$, n = 1).[122] In general, it appears that derivatives based on II are more stable than the analogous $C_5H_5^-$ containing species. An extreme example is $(HBpz_3)Cu(CO)$[123] which in the solid state decarbonylates only upon melting at 165°C whereas the corresponding $(C_5H_5)Cu(CO)$ is highly unstable except under an atmosphere of carbon monoxide and even then it decomposes within an hour at room temperature.

More recently the syntheses have been extended to include the early transition metals and the actinide metals as well. Thus, Manzer[124] has reported the preparation of complexes like $(C_5H_5)(HBpz_3)TiCl_2$, $(C_5H_5)_2Ti(HBpz_3)$ and $(C_5H_5)V(HBpz_3)$. The last complex is one member of a small class of mixed sandwich complexes as is the compound $[(C_5Me_5)Rh(HBpz_3)]^+$, synthesized by Lalor *et al.*[125] Bagnall *et al.*[126,127] have utilized the poly(pyrazol-1-yl)borate ligand system to form uranium derivatives; $U(H_nBpz_{4-n})_4$ (n = 1 or 2), $(C_5H_5)(HBpz_3)UCl_2$, and $(HBpz_3)_2UCl_2$. It is interesting to note that the $C_5H_5^-$ analogue of the last two complexes, $(C_5H_5)_2UCl_2$, cannot be prepared in pure form and attempted preparations of the bis(cyclopentadienyl) compound have resulted in $[(C_5H_5)_3U]_2[UCl_6]$[127] instead. This, once again, demonstrates the special stabilizing influence of the poly(pyrazol-1-yl)borate moiety.

From the preceeding paragraphs it can be seen that the chemistry of the ligand system introduced by Trofimenko is indeed wide in scope. Two areas however were conspicuous by their absence at the start of our research in this field, poly(pyrazol-1-yl)borate complexes of the lanthanide metals have not yet been synthesized nor were there examples of compounds with three poly(pyrazol-1-yl)borate ligands. Thus it was of interest to extend the poly(pyrazol-1-yl)-borate chemistry to include the lanthanide metals. It was also anticipated that, because of the propensity of the lanthanide ions for high coordination number and their larger size, tris complexes could be produced. This expectation received support from the synthesis of $U(HBpz_3)_4$ by Bagnall. In addition, since the analogy between $C_5H_5^-$ and $HBpz_3^-$ is well established, it was hoped that an extensive organolanthanide chemistry based on the $HBpz_3^-$ ligand could be obtained. This chapter describes the successful synthesis of lanthanide poly-(pyrazol-1-yl)borate complexes.[128] It also deals with organometallic derivatives for which the cyclopentadienide counterparts exist.

2. Hydrotris(pyrazol-1-yl)boratolanthanide(III) Complexes, $M(HBpz_3)_3$.

The interaction of $KHBpz_3$ and the hydrated lanthanide chlorides in water according to equation (V-1) precipitates

$$MCl_3 \cdot nH_2O + 3KHBpz_3 \xrightarrow{H_2O} M(HBpz_3)_3\downarrow + 3KCl \qquad \text{(V-1)}$$

$$M = La,\ Pr,\ Sm,\ Y,\ Er$$

the anhydrous $M(HBpz_3)_3$ complexes in nearly quantitative yields. The precipitated complex is isolated by filtration, washed with water and air dried. In this manner the La, Pr, and Sm complexes have been obtained directly with no apparent need for further purification as shown by satisfactory elemental analyses of the compounds. The Y and Er complexes had to be recrystallized from toluene/hexane solvent mixture to obtain analytically pure samples. In addition the corresponding Ce and Gd complexes were prepared and purified by prolonged Soxhlet extraction with CH_2Cl_2,[129] whereas the Yb and Lu derivatives were purified by crystallization from CH_2Cl_2.[130]

The $M(HBpz_3)_3$ complexes of the lanthanides are air stable in the solid state with elemental analyses remaining invariant over extended periods of time. In addition, they are thermally stable in air to 275°C without melting. The solubility of the complexes is very much dependent on the lanthanide ion. The heavy lanthanide derivatives are moderately soluble in THF and acetone, somewhat less in CH_2Cl_2 and have low solubility in toluene and benzene. The early lanthanide complexes are only sparingly soluble in any of the solvents listed above. However, the complexes can be dissolved only in dry solvents and the solutions must be handled under an inert atmosphere to avoid hydrolysis. The hydrolytically unstable nature of these complexes in solution was shown by the formation of pyrazole when solutions of the compounds were allowed to evaporate in air. Thus the anhydrous nature of the $M(HBpz_3)_3$ complexes from an aqueous reaction mixture is remarkable indeed. This would also suggest that these complexes will not behave as Lewis acids, differing in this regard from the corresponding tricyclopentadienide lanthanide complexes. To further confirm this lack of Lewis acidic character for the $M(HBpz_3)_3$ complexes, the reaction between anhydrous $PrCl_3$ and three equivalents of $KHBpz_3$ was carried out in dry THF under nitrogen. Again the unsolvated $Pr(HBpz_3)_3$ complex was obtained.

The $M(HBpz_3)_3$ compounds are all sufficiently volatile to obtain mass spectra, but they cannot be sublimed up to 220°C at 10^{-4} mmHg.

Mass spectra

The mass spectra of all the $M(HBpz_3)_3$ complexes clearly exhibit the parent ion, although in low abundance. In every case the most intense ion corresponds to the loss of one $HBpz_3$ ligand. The mass specta of the molecules are very rich but nevertheless the fragmentation process is relatively simple, dominated by losses of pyrazole moieties instead of internal fragmentation of the latter group. The relative intensities of the parent and a few other characteristic metal containing fragments are listed in Table 19. The formulation of the ions appearing in the table is suggested by the nature of the species lost to produce the given ion, and the fragmentation processes

Table 19. Relative intensities for some metal containing ions in the mass spectra of $M(HBpz_3)_3$ Complexes.[a]

M	Temp.	Ion $M[HBpz_3]_3^+$	$M[HBpz_3]_2[Bpz_2]^+$	$M[HBpz_3]_2^+$	$M[HBpz_3][Bpz_2]^+$	$M[HBpz_3][pz]^+$	$M[Bpz_3]^+$	Mpz_2^+
La	210°	3	16	100	1	49	2	36
Pr	205°	2	13	100	1	56	4	52
Sm	200°	<.1	2	100	7	51	7	39
Y	160°	1	4	100	2	28	5	12
Er	145°	2	3	100	2	32	6	10
Yb[b]	180°	1	15	100	23	53	16	14
Lu[b]	175°	.3	14	100	21	51	13	18

[a] Ionizing voltage = 70 eV.

[b] Ref. 130.

are in turn supported in most cases by the observation of the corresponding metastable peaks. The metastable peaks so observed are listed in Table 20.

It is tempting to consider the data in the Tables and to separate the $M(HBpz_3)_3$ complexes into groups as a funtion of intensities of fragment ions and breakdown patterns suggested by metastable peaks. This was previously done for the mixed sandwich complexes. However, the present data does not appear to be amenable to simple clear cut divisions. For instance, the complexes with La and Pr might be expected to be quite similar and to typify complexes with the early lanthanides. Although the intensities of the fragment ions seem to bear out this expectation, the La complex curiously exhibits only two metastable peaks in contrast to the seven metastable peaks observed for the Pr derivative. This might suggest some difference in the decomposition of the La complex in the mass spectrometer. Also the mass spectra of the Sm and Yb complexes might be expected to resemble one another due to the available 2+ oxidation states, since this was seen before to be responsible for the particular intensities of the fragment ions observed in the spectra of the mixed sandwich complexes. Inspection of the tables does not reveal this similarity for the hydrotris(pyrazol-1-yl)borate complexes for these two metals. Finally, the Y, Er, and Lu complexes should

Table 20. Calculated values of the metastable peaks corresponding to the major fragmentation processes observed in the mass spectra of $M(HBpz_3)_3$ complexes.

	Metastable Peak						
Fragmentation Process	La	Pr	Sm	Y	Er	Yb[a]	Lu[a]
$M(HBpz_3)_3^+ \rightarrow M(HBpz_3)_2(Bpz_2)^+ + Hpz$	647.9	649.9	-	598.3	674.5	682.7	683.6
$M(HBpz_3)_3^+ \rightarrow M(HBpz_3)_2^+ + HBpz_3$	-	412.7	-	364.3	435.3	-	443.7
$M(HBpz_3)_2(Bpz_2)^+ \rightarrow M(HBpz_3)_2^+ + Bpz_2$	449.6	451.5	462.0	401.8	475.5	483.2	484.2
$M(HBpz_3)_2^+ \rightarrow M(HBpz_3)(Bpz_2)^+ + Hpz$	-	439.1[b]	-	387.9	463.8	471.7	472.6
$M(HBpz_3)_2^+ \rightarrow M(HBpz_3)(pz)^+ + HBpz_2$	-	312.6	322.8	264.3	336.0	343.5	344.5
$M(HBpz_3)(pz)^+ \rightarrow M(Bpz_3)^+ + Hpz$	-	295.9	306.7	245.5	320.3	328.1	329.1
$M(Bpz_3)^+ \rightarrow M(pz)_2^+ + Bpz$	-	214.2	-	165.2	238.1	-	246.7

[a] Ref. 130.

[b] Very weak.

typify the spectra for complexes with the later lanthanides. Even though Y and Er appear quite similar, the Lu complex exhibits a distinctly different intensity pattern, which in fact, is quite similar to that of the Yb analogue.

Though small differences do exist in the comparison of the mass spectra data for the compounds at hand, what is in fact more striking is the rather similar nature of the spectra for all the complexes so far considered.

Infrared and Raman spectra

The infrared spectra of the $M(HBpz_3)_3$ compounds, with the possible exception of the B-H stretching region of the Er, Y, Yb, and Lu derivatives are similar to those observed for other metal poly(pyrazol-1-yl)borate complexes. The spectra are rather complex in the 600-1600 cm^{-1} region and exhibit characteristic absorption(s) at ca. 2450 cm^{-1} assignable to the B-H stretching vibrations(s).[118] Examples of the spectra for an early and late lanthanide complex along with that of the potassium salt of the ligand are given in Figure 13 for the two regions just mentioned.

Inspection of Figure 13 shows that there are some differences in the spectra of the praseodymium and erbium complexes. The most strking difference is in the B-H stretching region. The Pr complex displays a very sharp absorption of medium to strong intensity at

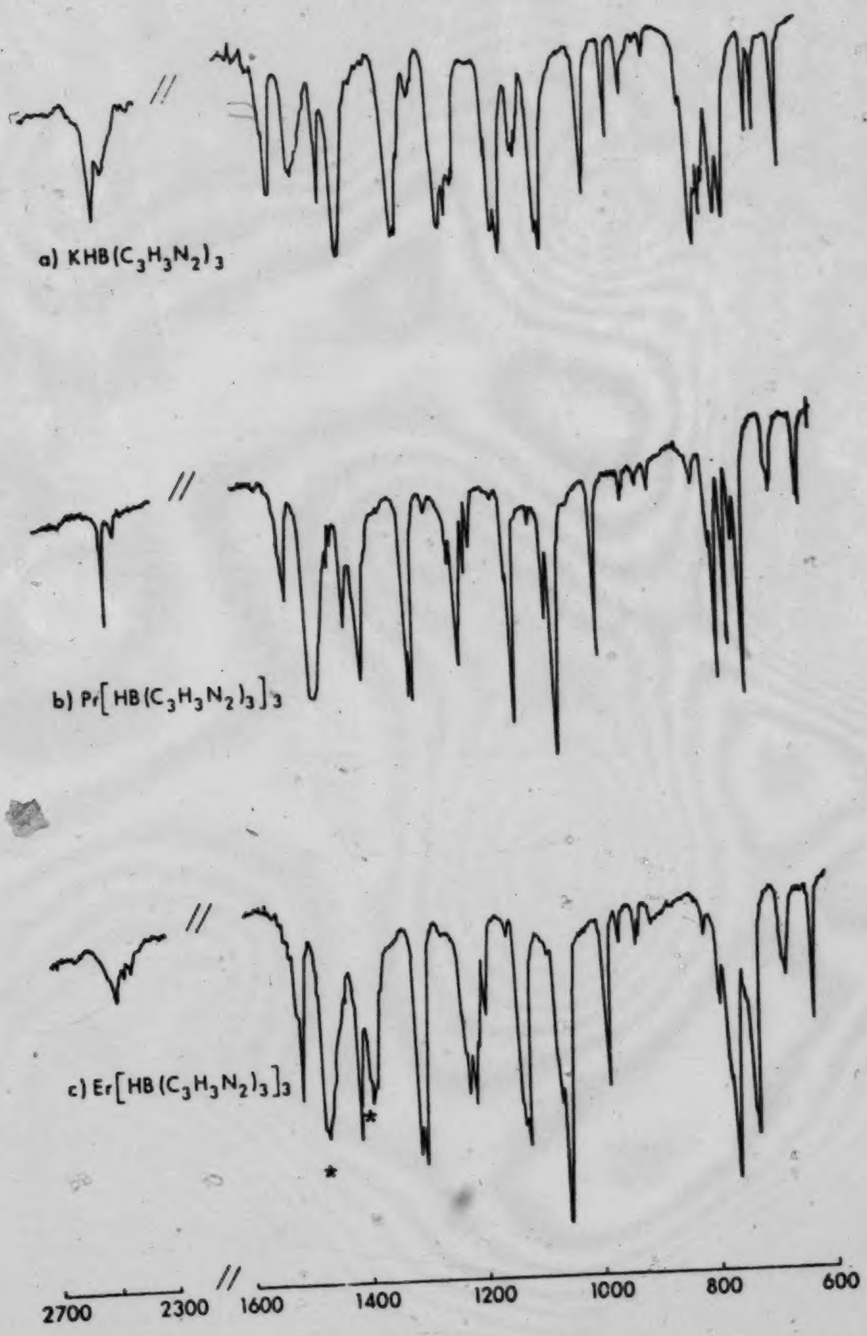


Figure 13. Infrared spectra of $M(HBpz_3)_3$ complexes (M = Pr, Er) and $KHBpz_3$. Recorded as mineral oil, (*), mulls. Note the band at ca. 1380 cm^{-1} primarily contains absorption due to the complex.

2447 cm^{-1} and a weak band at 2412 cm^{-1}, whereas for the Er complex this region is comprised of four weak bands from 2498 to 2422 cm^{-1}. It is interesting to note that mention of multiple B-H stretching absorptions have not been made in previous reports on poly(pyrazol-1-yl)-borate complexes. Additional variations occur in the 770 to 720 cm^{-1} region, in that the Pr complex exhibits three sharp, distinct bands whereas the erbium derivative shows two strong bands in this region. Less obvious differences occur at ca. 1220 cm^{-1} where an intensity variation exists and at ca. 625 cm^{-1} where the band is split into two components for praseodymium and remains sharp for the erbium complex. Although only very weak bands occur at 960 to 880 cm^{-1} the different pattern of absorption in this region also appears to be indicative of the particular metal. These differences are pointed out here because the compounds so far examined by infrared spectroscopy can be placed into two groups based on these spectral variations. The La, Pr, and Sm derivatives comprise one group, their spectra being nearly superimposable. Similarly, the Er, Y, Yb and Lu compounds form a second group. A more complete comparison of these groups can be obtained by examining the bands listed in Table 21 for the $M[HBpz_3]_3$ complexes.

It is tempting to ascribe the variations in the infrared spectra, especially the strikingly different

Table 21. Partial infrared spectra of $M[HBpz_3]_3$ complexes and $K[HBpz_3]$.[a,b]

La	Pr	Sm	Er	Y	Yb[c]	Lu[c]	L
			2498vw		2490vw	2496w-m	
2448m-s	2447m-s	2443m-s	2476w	2475vw	2475w	2475w	2448m
			2448w	2438vw	2442w	2448w	2415w-m
2411w	2412w	2411w	2422vw	2415w	2419vw	2420w	
1381s	1382s-m	1381s	1386m-s	1385s	1387s	1390s	1392s
1300s	1301s	1303vs	1306s	1304s	1307s	1306s	1302s
1294s	1293s	1293vs	1298s	1299s	1300s	1299s	1292s
1227m-w	1229m-w	1230m	1220m	1227m	1225m	1223m-s	1222sh
1214s	1217s	1217s	1210m-s	1215m	1214m	1211m	1215s
1048vs	1047s	1045vs	1052s	1049s	1054s	1056s	1049s
975s	973s	975s	980s	978s	980s	985s	966s
			959w	956w	956w	963w	
928w	926w	925w	929w		927w	933w	923m
900w	900w	902w	924vw	924w,br	921vw	928w	900w
882w	878w	879w	900vw	899vw	901vw	900w	
						890vw	858w
							780s
770s	768s	768s	760s	758s	757s	758s	772m
							765m-s
753s	751s	753vs	729sh		730s	729s	750s
727s	722s	724vs	725s	724s	725s	726s	725s
628wpm	626w-m	625w-m	627m	623m	625m-s	625m-s	635m-s
622w-m	621w-m	620w-m					

[a] Frequencies in cm^{-1}. Recorded as mineral oil mulls. [b] Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

[c] Ref. 130.

B-H stretching region, to the occurrence of a change in solid state structure of these tris complexes as one proceeds from the early to the late lanthanide metals. The structure of the $Yb(HBpz_3)_3$ complex has been determined by a single crystal X-ray diffraction analysis.[130] The structure is shown in Figure 14. The Yb is surrounded, in a bicapped trigonal prismatic array, by eight pyrazole nitrogens from two tridentate and one bidentate $HBpz_3$ ligand. The low symmetry, at most C_s, of the complex is consistent with the complicated B-H stretching region seen in the infrared spectrum. Extending this argument, the simpler B-H stretching pattern of the early lanthanide complexes should reflect a more symmetrical solid state structure. Unfortunately, the very low solubility of the early lanthanide metal derivatives has so far thwarted attempts to obtain crystals suitable for an X-ray study which would make it possible to verify the implied structural differences between these two groups of complexes. However, the different solubility behavior for the two groups of complexes is further evidence for the suggested difference in structure.

The Raman spectra of the complexes also exhibits differences between the early and late lanthanide derivatives and further corroborate the conclusions reached above based on infrared spectral data. The spectra of the Pr and Er complexes are shown in Figure

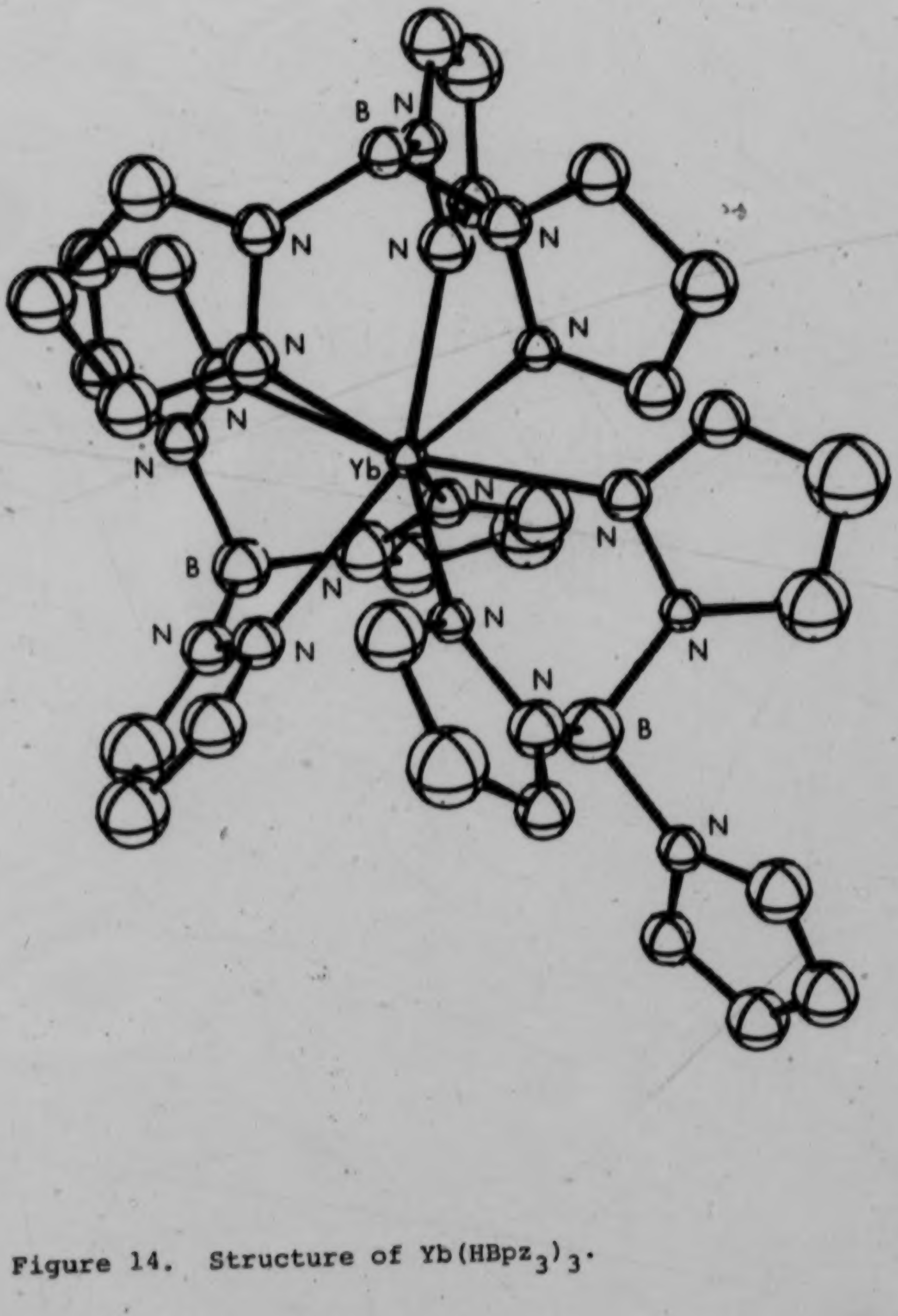

B
N
N
N
N
N
N
N
Yb
N
N
B
N
N
N
N
N
N
B
N

Figure 14. Structure of $Yb(HBpz_3)_3$.

15a and 15b respectively. For the early lanthanide complexes a very weak, broad ν(B-H) appears at ca. 2445 cm^{-1} while for complexes with the heavier lanthanides a weak multiple ν(B-H) absorption occurs between 2425-2485 cm^{-1}. The three bands in the 1210 to 1400 cm^{-1} region exhibit similar intensity patterns depending on whether the complex contains an early or late lanthanide metal. Two bands appear at 1100 and 1125 cm^{-1} in the early lanthanide complexes whereas a more complex band with a sharp peak at ca. 1110 cm^{-1} is seen with the later lanthanides. Also, a minor variation is apparent in the weak and very weak bands in the 670-790 cm^{-1} region. This is more easily seen by reference to Table 22 which lists the bands so far mentioned and other prominent bands in the Raman spectra of the $M(HBpz_3)_3$ complexes. Finally the Raman spectrum in the 125 to 400 cm^{-1} region, for the Pr complex (Figure 16a) and for the Lu complex (Figure 16b) also appear qualitatively different. This again would not be unexpected should the $M(HBpz_3)_3$ complexes belong to different structural classes depending on the central metal involved.

NMR spectra

The ^1H NMR spectrum of the starting potassium salt, $KHBpz_3$, exhibits a simple spectrum comprised of two doublets and a triplet in the intensity ratio 1:1:1. In

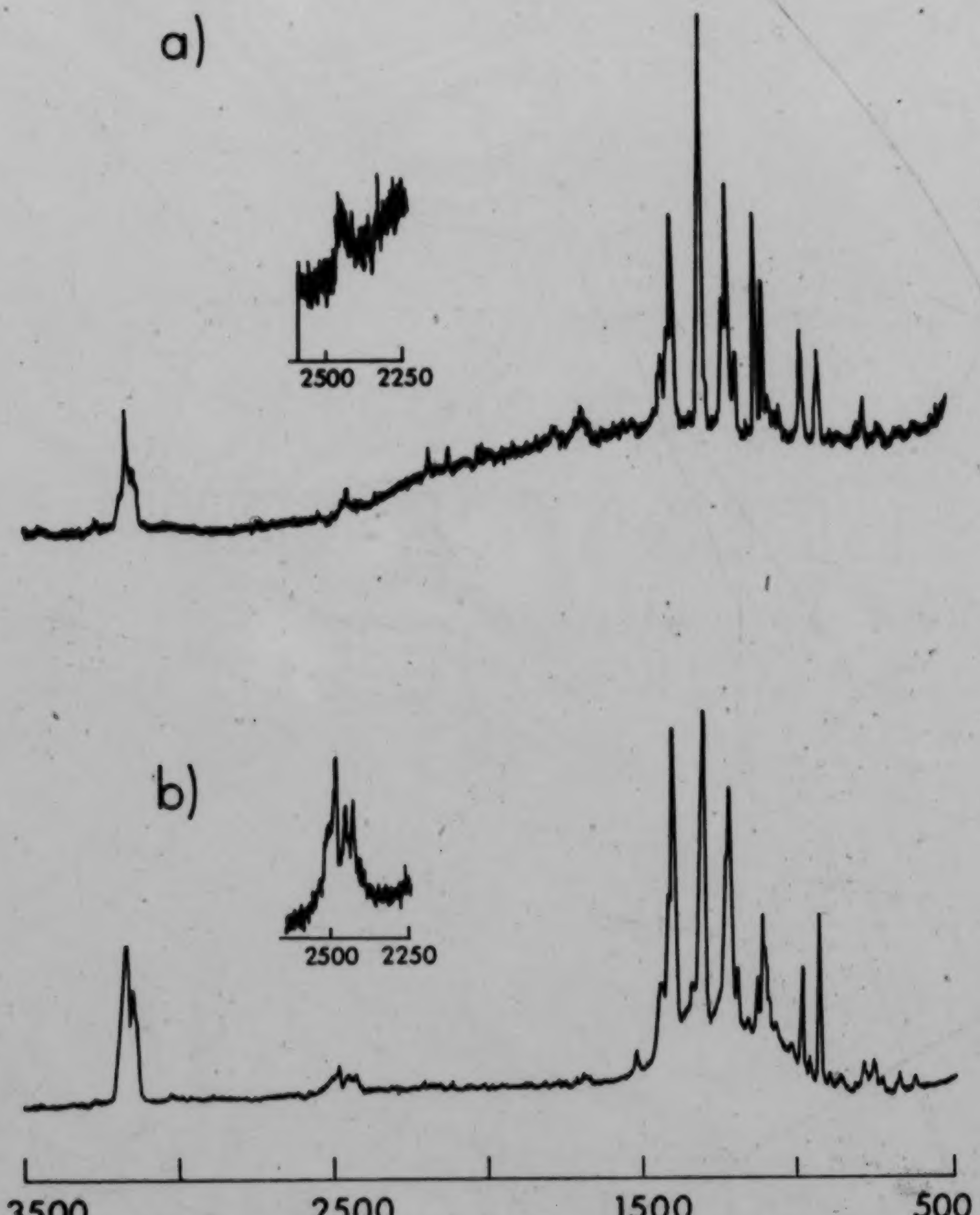


Figure 15. Raman spectrum of $M(HBpz_3)_3$.

a) M = Pr, b) M = Er.

Table 22. Raman Spectra of $M(HBpz_3)_3$ complexes and $KHBpz_3$.[a]

La	Pr	Sm	Y	Er	Yb	Lu	K
3170m	3166m	3166m	3170m-s	3170m	3170m	3169m	3165w-m
3146w-m	3142w		3150m	3150m	3149m	3149m	3151w
				2488w	2485w	2484w	3120w
2446vw	2441vw	b	2469w	2457vw	2450w	2454w	2444w
			2425vw	2432vw	2428vw	2426vw	2412w
1398m	1392m	1396m	1402s	1400s	1401s	1402s	1409s
1300s	1295s	1301s	1305s	1307s	1305s	1306s	1304s
1215m	1209m	1216m-s	1223m-s	1219m-s	1217m-s	1218m-s	1223s
1130s	1124m	1126m	1105m	1111m	1116m	1112m	1097m
1103m	1098m	1097m	-	-	-	-	1066m
980m	975m	978m	985m	986m	989m	989m	977m
925m	921m	916m	930m	930m	932m	931m	934m
780w	776w	788w	783w	787w	787w	784w	794w
725vvw	726vvw	743vw	750w	749w	758w	-	769w
670vvw	666vvw	678vvw	677vw	670vw	679vw	-	682w
-	-	628vvw	625vvw	620vvw	625vvw	624vvw	634w

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[a] Recorded on solids in sealed capillaries; frequencies in cm^{-1}; abbreviations as in Table 21.

[b] Region obscured by lasers or fluorescence.

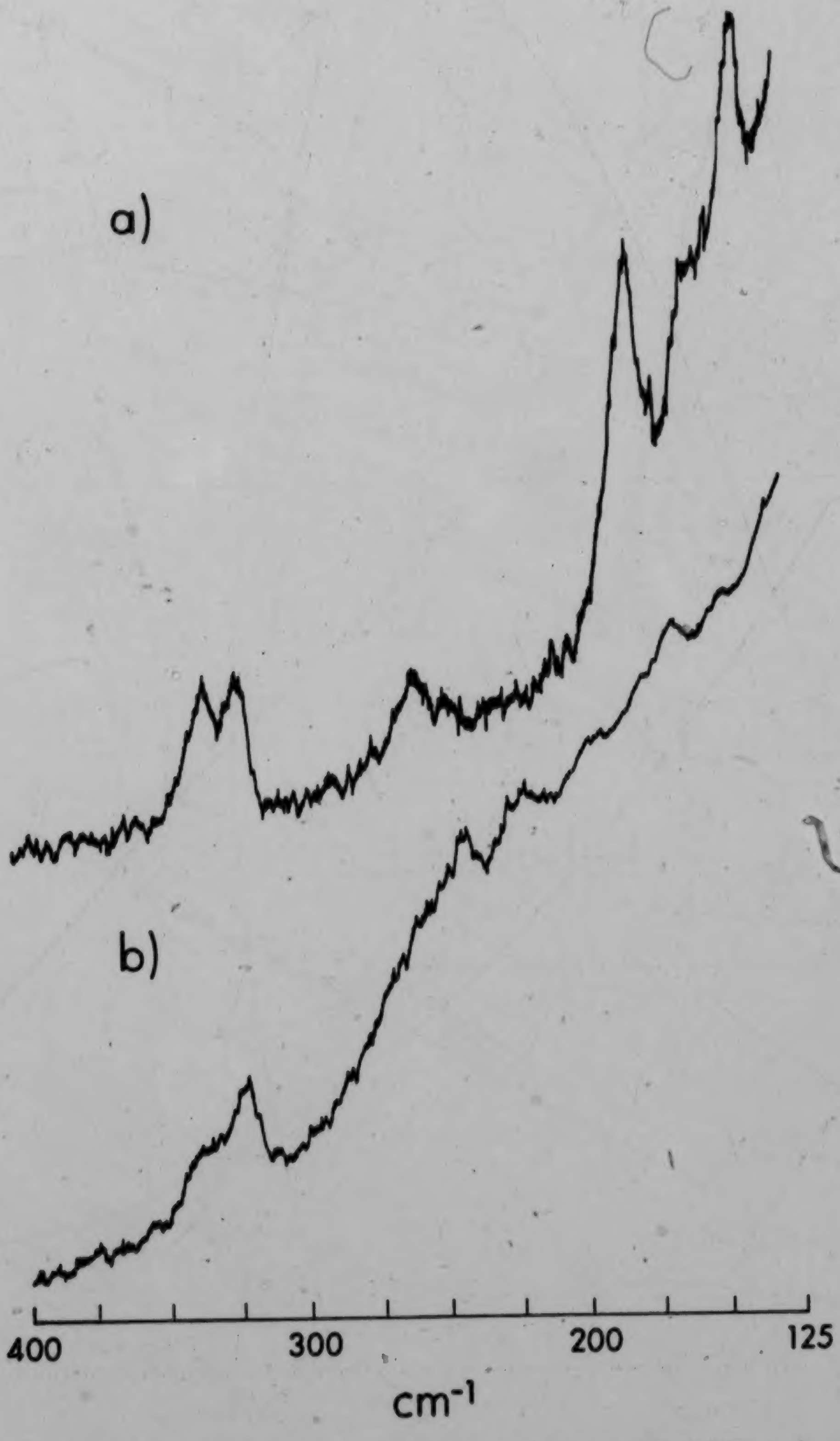

Figure 16. Low frequency Raman spectrum of M(HBpz$_3$)$_3$:

a) M = Pr, b) M = Lu.

D_2O these resonances occur at δ7.74(d), 7.46(d), and 6.39(t) assigned to the protons in the 5, 3, and 4 positions (for notation see diagram I, p. 140) of the three identical pyrazolyl residues, respectively.[118]

The ^1H NMR spectrum of $Y(HBpz_3)_3$ recorded in CD_2Cl_2 exhibits several poorly resolved resonances which fall in two regions at δ5.1-6.0 ppm and δ7.15-8.0 ppm. Upon cooling to -50°C there are some minor changes in the resonance positions and some improvement in resolution such that doublet structure of some of the peaks in the low field region is now evident. Nevertheless, the complexity of the spectrum has not permitted a proper assignment. It was argued, based on the infrared spectrum of the yttrium compound, that its structure probably resembles that of the ytterbium derivative shown in Figure 14. The low symmetry of the structure demonstrates that a complex ^1H NMR spectrum for these complexes is not unexpected.

The low solubility of the $M(HBpz_3)_3$ compounds with the early lanthanides has prohibited the recording of their ^1H NMR spectra.

3. Hydrotris(pyrazol-1-yl)borato(chloro)lanthanide(III) complexes, $(HBpz_3)_nMCl_{3-n}\cdot xTHF$, n = 1 and 2.

The interaction of the anhydrous lanthanide chloride with stoichiometric amounts of $KHBpz_3$, eq. (V-2), in dry

$$MCl_3 + nKHBpz_3 \xrightarrow{THF} (HBpz_3)_nMCl_{3-n}\cdot xTHF + nKCl \quad (V-2)$$

$M = Er, Y;\ n = 2;\ x = 1$

$M = Er,\ \ n = 1;\ x = 1.5$

THF under an atmosphere of prepurified nitrogen yields the mixed hydrotris(pyrazol-1-yl)borato(chloro)lanthanide(III) complexes upon crystallization from THF/hexane mixtures at -20°C. Using the same procedure the corresponding Yb and Lu complexes were also synthesized.[130] The formulation of the complexes is supported by elemental analysis.

Complications arose when the synthesis was extended to the early lanthanides. With Pr and Ce the pure compounds could not be isolated, mixtures of materials seemed to form. This is reminiscent of the behavior of the early lanthanide metals with the $C_5H_5^-$ ligand in Dubeck's[16,17] attempt to prepare monocyclopentadienide and dicyclopentadienide complexes.

The solid mixed hydrotris(pyrazol-1-yl)borato(chloro) complexes readily hydrolyze in air in contrast to the $M(HBpz_3)_3$ complexes. Also, as indicated in eq. (V-2), the complexes are obtained with coordinated THF as opposed to the $M(HBpz_3)_3$ compounds. The coordinated THF is evident in the ^1H NMR, infrared, and mass spectra of these compounds.

Mass Spectra

The mass spectra of the $(HBpz_3)_2MCl\cdot THF$ complexes exhibit a weak parent ion with the $(HBpz_3)_2M^+$ fragment being the most abundant metal containing ion. In general, metastable peaks are not seen in these spectra. This is in contrast to the $M(HBpz_3)_3$ complexes where the fragmentation processes could usually be verified by the appropriate metastable ions. Characteristic metal containing fragments are listed in Table 23. In both complexes very strong ions occur at m/e 72 and 71 which correspond to THF in the compounds. The spectra of the two complexes are quite similar to one another with the exception of the intensity of the $(pz)_2M^+$ fragment. There is no ready explanation for this difference.

The mass spectrum of the $(HBpz_3)ErCl_2\cdot 1.5THF$ complex is not particularly informative. Instead of exhibiting the parent ion, $(HBpz_3)_2ErCl^+$ is observed followed by the normal fragment ions found in the $(HBpz_3)_2ErCl\cdot THF$ spectrum. A similar observation was made for the Lu derivative.[130] It is interesting to note that attempts to obtain the mass spectrum of $(C_5H_5)HoCl_2\cdot 3THF$ also do not yield the expected parent ion but rather give the $[(C_5H_5)_2HoCl]_2^+$ ion.

Infrared spectra

The infrared spectra of the $(HBpz_3)_nMCl_{3-n}\cdot xTHF$ complexes are also quite complex in the 600-1600 cm^{-1}

Table 23. Relative intensities of characteristic metal containing ions in the mass spectra of $(HBpz_3)_2MCl \cdot THF$ complexes.

Ion	Er(165°C)	Y(185°C)
$(HBpz_3)_2MCl^+$	4	4
$(HBpz_3)_2M^+$	100	100
$(HBpz_3)(Bpz_2)MCl^+$	8	9
$(HBpz_3)M(pz)^+$	33	41
$(Bpz_3)MCl^+$	14	20
$(Bpz_3)M^+$	5	7
$(pz)_2M^+$	19	37
$(pz)MCl^+$	4	9

region and bear some resemblance to the corresponding $M(HBpz_3)_3$ derivatives. However, some notable differences are apparent. Characteristic bands for these complexes are listed in Table 24.

Inspection of the Table and comparison to the data in Table 21 for the respective $M(HBpz_3)_3$ complexes shows a considerable difference in the B-H stretching region. The $(HBpz_3)_nMCl_{3-n}$ derivatives have a relatively sharp, strong to medium intensity ν(B-H) absorption in contrast to the weak multiple B-H stretching absorptions in the respective tris complexes. The sharpness of this absorption in the $(HBpz_3)_2MCl \cdot THF$ complexes probably indicates a relatively symmetrical arrangement of the poly(pyrazol-1-yl)borate moieties in the solid state. A similar proposal was made in comparing the B-H stretching region of the $M(HBpz_3)_3$ complexes for the early and late lanthanides, the sharp B-H stretch in the early lanthanide complexes was taken to suggest a more symmetrical arrangement of the ligands than in the later lanthanide derivatives.

Returning to the data in Table 24, the bands at 885 and 880 cm^{-1} in the monochloro complexes and the band at 863 cm^{-1} in the dichloro derivatives are assigned to absorption due to coordinated THF. Also the band at 1018 cm^{-1} in the dichloro complex appears to be due to THF, but it is not clear where this absorption occurs in the $(HBpz_3)_2MCl \cdot THF$ complexes. A band at *ca*. 1048 cm^{-1}

Table 24. Partial infrared spectra of $(HBpz_3)_nMCl_{3-n}\cdot xTHF$ Complexes.[a]

$(HBpz_3)_2ErCl\cdot THF$	$(HBpz_3)_2YCl\cdot THF$	$(HBpz_3)ErCl_2\cdot 1.5THF$
2468s,sharp	2470m-s,sharp	2503sh
		2473m
1384s	1385s	1383s
1302sh		
1297s	1300s	1293s
1218sh		
1213s	1210s	1213s
1054sh	1053sh	
1048vs	1046vs	1043s
		1018m
975m-s	979s	978s
933w	930w	
924w	925w	
921w		924w
913w		921w
		902w
		897w
885m	880m	863m-s
		773s
753s	760s	
		762s
733m	735m-s	735m
722s	724s	722s
		715s
618m-s	620m-s	
		621s
604w	609w	

[a] Frequencies in cm^{-1}; recorded as mineral oil mulls; abbreviations as in Table 23.

is slightly broadened and asymmetric for both complexes, and could represent contributions from ligand and coordinated THF vibrations. This assignment is not firm because the ligand itself absorbs at this position. However, the bands in the 885-860 cm^{-1} region for the three complexes in Table 24 are in an area free of other ligand absorptions and can be confidently attributed to THF. These band positions for the monochloro complexes are similar to those for the THF adducts of the mixed sandwich compounds (see Table 11) and, as suggested before, represent a significant but relatively weak M-O interaction. On going to the dichloro derivative the frequency of this band is lowered by ca. 20 cm^{-1} indicating an increase in the strength of the M-O bond. It is interesting to note that the infrared spectrum of $(C_5H_5)ErCl_2 \cdot 3THF$, recorded in this laboratory, exhibits a band at 860 cm^{-1} attributed to THF. The higher frequency band appears to be coincident with or on the side of the very strong absorption due to the C_5H_5 ring at 1015 cm^{-1}.

NMR spectra

The ^{1}H NMR spectrum was recorded for the diamagnetic $(HBpz_3)_2YCl \cdot THF$ complex in CD_2Cl_2. Unfortunately, the spectrum contained an impurity (a doublet at δ7.3 and a triplet at δ6.2 in the ratio 2:1). Nevertheless, the spectrum did display the expected pattern for symmetrically bonded tridentate poly(pyrazol-1-yl)borate ligands (doublets at δ7.7 (2 Hz) and 7.0 (2Hz), apparent triplet at δ6.0 (2 Hz) in the ratio 6.1:6.0:6.0). In addition multiplets for THF are observed at δ3.7 and δ1.8 but integrate only to ca. 0.89 THF molecules in the complex. This spectrum does compare favorably to the analogous lutetium derivative which did not initially exhibit bands in addition to the desired complex,[130] (doublets at δ7.6 (2 Hz) and 7.1 (2Hz), apparent triplet at 6.0, THF resonances at δ3.6 and 1.7 in the ratio 6:6:6:3.5:3.5). However, with time, in the spectrum of this sample, sealed *in vacuo*, also there appear a doublet and triplet at δ7.3 and δ6.2 respectively in the ratio 2:1.

4. Reactivity of hydrotris(pyrazol-1-yl)borate(chloro)lanthanide(III) complexes with organometallic reagents.

i) $K_2C_8H_8$

Interaction of stoichiometric amounts of $K_2C_8H_8$ and $(HBpz_3)MCl_2\cdot1.5THF$, eq. (V-3), at -40°C produces the

$$(HBpz_3)MCl_2\cdot 1.5THF + K_2C_8H_8 \xrightarrow[-40°C]{THF} (HBpz_3)M(C_8H_8) + 2KCl \qquad (V-3)$$

M = Er, Lu

"mixed sandwich" complex $(HBpz_3)M(C_8H_8)$ isolated by crystallization after filtration to remove KCl.

The complexes are soluble in THF and pyridine. As expected, the compounds are air and water sensitive but they are not pyrophoric as are the base free $(C_5H_5)M(C_8H_8)$ complexes. However, this difference may be a result of the nature of the products obtained with the two materials; well formed crystals with $(HBpz_3)M(C_8H_8)$ and powdery solids with the $(C_5H_5)M(C_8H_8)$ derivatives.

Mass spectra

The mass spectra of the Er and Lu complexes exhibit the parent ion as the most abundant metal containing ion and there is no indication of THF in the spectrum. Fragmentation of the complexes in the mass spectrometer reflects the presence of both ligands in the compounds. Characteristic metal containing ions are listed in Table 25.

Inspection of the table shows no ion corresponding to $C_8H_8M^+$ which was a significant feature of the spectrum of the mixed sandwich compounds discussed in Chapter II. However, the fragment ion, $(HBpz_3)M^+$, is the second most abundant ion in the spectrum. It thus appears from the limited data at hand that the bonding between the poly(pyrazol-1-yl)borate ligand and the metal is stronger than the corresponding interaction with the cyclooctatetraenide moiety.

Additional fragmentation is characteristic of the individual ligands. The loss of acetylene from the

Table 25. Relative intensities of metal-containing ions in the mass spectra of $(HBpz_3)M(C_8H_8)$ complexes.

Ion	Er(145°C)	Lu(150°C)
$(HBpz_3)M(C_8H_8)^+$	100	100
$(HBpz_3)M(C_6H_6)^+$	~1	2
$(Bpz_2)M(C_8H_8)^+$	3	6
$(HBpz_3)M^+$	48	41
$(pz)_2M^+$	29	26
$(HBpz_3)MC_8H_8^{2+}$	2	2
$(pz)M^+$	14	6
M^+	3	3

bound C_8H_8 ligand was seen in Chapter II (a metastable peak corresponding to this fragmentation process was clearly observed for erbium but was so weak in the lutetium complex that its observation was questionable) whereas the loss of Hpz and pz were common features of the $M(HBpz_3)_3$ complexes.

Infrared spectra

The infrared spectra of the $(HBpz_3)M(C_8H_8)$ complexes, listed in Table 26, again display the sharp B-H stretching absorption characteristic of the symmetrical arrangement of the poly(pyrazol-1-yl)borate moiety. The spectra are complex in the 600-1600 cm^{-1} region and strongly resemble one another. In addition the spectrum of the $(HBpz_3)$-$ErCl_2 \cdot 1.5THF$ complex (Table 24) and the $(HBpz_3)Er(C_8H_8)$ derivative gave very similar absorptions attributable to the $HBpz_3$ ligand. One notable exception does occur. The band at 1213 cm^{-1} in the former complex appears as two bands at 1205 and 1192 cm^{-1} in the latter complex. Since the origin of this band is unknown only this qualitative observation can be made.

A more important region of the infrared spectrum in organolanthanide complexes containing the C_8H_8 ligand, as we have previously shown, is 690-730 cm^{-1}. In this area should be found the absorption due to the out-of-plane C-H bending mode. Although this region of the

Table 26. Partial infrared spectra of $(HBpz_3)M(C_8H_8)$ Complexes.[a]

Er		Lu	
2503vw		2505vw	
2463m,sharp	777s	2466m,sharp	782s
2418vw	763s		769s
	733m		732m
1389sh	730m	1388s	726m
1381s	714s	1381s	721s
1297s	703s	1302s	707s
1205s	698sh	1211s	702s
1192s-m	618sh	1195m-s	621m
	613m-s		618m
1047s		1052s	
974s		982s	
887m-s		890m-s	

[a] Frequencies in cm^{-1}; recorded as mineral oil mulls; abbreviations as in Table 23.

spectrum is rich in absorption due to the $HBpz_3$ moiety, bands at 703s/698sh cm^{-1} in the Er complex and at 707s/702s cm^{-1} in the Lu derivative appear to belong to this mode. As we have argued in Chapter II the lower the frequency of this mode the greater the degree of electrostatic character in the metal-ring interaction. A comparison of these band positions to those for the respective $(C_5H_5)M(C_8H_8)$ complexes in Table 3 shows a decrease of some 12-15 cm^{-1}. This would suggest a greater degree of ionic character in the metal-C_8H_8 ring interaction in the $(HBpz_3)M(C_8H_8)$ complexes than in the mixed sandwich compounds. This might imply that the $HBpz_3^-$ ligand functions as a slightly better donor of electron density than the $C_5H_5^-$ ligand in these compounds. Of course this requires the assumption that both types of mixed sandwich complexes have a relatively symmetrical arrangement of the ligands so that no unusual solid state effects might be present and affect this mode.

To return to the data in Table 26, the band at ca. 890 cm^{-1} is assigned to the in-plane C-H bending mode and falls in the expected region for complexes with the C_8H_8 ligand. Attempts to locate the asymmetric C-C stretching vibration were hampered by absorption in the 1430-1440 cm^{-1} region by the $HBpz_3$ ligand.

NMR spectra

The ^{1}H NMR spectrum of the lutetium derivative, exhibiting the characteristic two doublets and a triplet, clearly indicates the symmetrical arrangement of the poly(pyrazol-1-yl)borate ligand within the complex. In addition the spectrum also contains a sharp singlet due to the symmetrically bound cyclooctatetraenide moiety. The chemical shift data for $(HBpz_3)Lu(C_8H_8)$ in pyridine-d_5 are, δ8.05 d, δ7.64 d, δ7.02 s and δ6.10 t in the expected intensity ratio 3:3:8:3.

The most striking feature of the ^{1}H NMR spectrum is the low field of the C_8H_8 resonance. This is considerably lower than the value δ6.2 observed for the C_8H_8 resonance in $(C_5H_5)Lu(C_8H_8)$ (toluene-d_8 or pyridine-d_5). Such a low field chemical shift was not anticipated for the $(HBpz_3)Lu(C_8H_8)$ derivative based on the infrared data just noted. However, we have seen before that the chemical shift in these organolanthanide derivatives appears to be controlled by several factors and does not always respond to the simple idea of changing electron density on the ring as suggested by the infrared data in the solid state.

The chemical shift of the poly(pyrazol-1-yl)borate moiety is shifted from that in the starting complex[130] (acetone-d_6: δ7.87 d, δ7.73 d, δ6.17 t), and there is a change in the chemical shift difference between the protons at the 3 and the 5 positions. Trofimenko has shown that the chemical shifts and the separation between the resonances are both solvent and cation dependent in M(HBpz$_3$), M = Li, Na, K, Cs. Thus the above observations are not surprising and could reflect partly the change in bonding upon replacing two chloride ions with the $C_8H_8^{2-}$ ligand.

Visible spectrum

The electronic spectrum of the (HBpz$_3$)Er(C_8H_8) complex was recorded in tetrahydrofuran and qualitatively appears to be quite similar to that of the (C_5H_5)Er(C_8H_8) derivative. The bands in the visible region for the two complexes are listed in Table 27. Again a charge transfer band tails into the visible region as seen for the mixed sandwich compound and difficulties similar to those noted previously were encountered in attempting to locate the maximum of this absorption.

The band progression observed for the poly(pyrazol-1-yl)borate complex from 520-555 nm strikingly resembles that observed in the mixed sandwich compound. The intensity of the bands in this region is only slightly less than for the (HBpz$_3$)Er(C_8H_8) complex. It appears that the central metal in these two complexes is in a comparable environment.

The small differences in band position between these two complexes might suggest that a slightly greater red

Table 27. Visible spectrum of $(HBpz_3)Er(C_8H_8)$ and $(C_5H_5)Er(C_8H_8)$ in THF.[a]

$(HBpz_3)Er(C_8H_8)$		Assignment	$(C_5H_5)Er(C_8H_8)$	
λ	ε		λ	ε
			493	9
		$^4F_{7/2}$	496	13
492	4		498	10
495	3		501	7
519	12			
522	33			
524	10	$^2H_{11/12}$	527	44
528	16		529	31
531	6		533	24
533	3		536	18
537	5		539	14
539	2	$^4S_{3/2}$	543	11
542	4		547	10
545	3		549	9
553	10		554	10
555	4		557	7

---

[a] Wavelength in nm.

shift of the f-f transitions occurs in the $(C_5H_5)Er(C_8H_8)$ compounds. However, as we mentioned in Chapter III, quantitative comparison requires knowledge of the ground state splitting and assignment of excited state levels. A difference of 3-5 nm is too small to provide a firm basis for discussion of changes in the electronic spectrum when the C_5H_5 ligand is replaced by the $HBpz_3$ moiety.

ii) Reactions with other organometallic reagents.

We have established that the $(HBpz_3)MCl_2 \cdot 1.5THF$ complexes react in a similar fashion with $K_2C_8H_8$ as does the cyclopentadienide analogues. It was hoped that, as shown for the analogous cyclopentadienide derivatives by Tsutsui,[46] the chloride ions could be exchanged with anionic organic moieties providing a new class of σ-bonded organolanthanide complexes.

Reactions were tried first with $Mg(CH_2SiMe_3)_2$, LiMe, LiPh, $C_6H_5CH_2MgCl$ and the monochloro and dichloro poly(pyrazol-1-yl)borate derivatives. These reactions were carried out in the usual manner by adding the stoichiometric amount of the organometallic reagent to a solution of the poly(pyrazol-1-yl)borate complex. The reactions did not yield the desired complex in any case. The most readily identified product in these reactions was the corresponding $M(HBpz_3)_3$ (infrared and mass spectrometry) and in some cases the respective RH compound

(NMR spectrometry) was identified. Other metal containing compounds could not be identified. There is no ready explanation for the course of these reactions. However, it was felt that the drive for higher coordination numbers in the lanthanide series might be responsible for the observation of $M(HBpz_3)_3$ as a reaction product. If such a problem existed, it was hoped that the use of a ligand capable of occupying more than one coordination site might result in stable, isolable complexes. The reaction of o-lithio-p-tert-butyl-N,N-dimethylbenzylamine with $(HBpz_3)_2ErCl \cdot THF$ was carried out in the hope that the nitrogen in the amine ligand would act as a donor to the erbium. Then chelate formation would stabilize the desired complex. Once again $Er(HBpz_3)_3$ was identified as a product of the reaction as well as the parent amine.

A different route then was tried to obtain organolanthanide derivatives containing the poly(pyrazol-1-yl)-borate moiety. Instead of starting with the $(HBpz_3)_2$-$MCl \cdot THF$ derivative, the $(C_5H_5)MCl_2 \cdot 3THF$ complex was used and $KHBpz_3$ was reacted with it. In reactions with M = Sm, Er, Yb and the stoichiometric quantity of $KHBpz_3$, the tris complex, $M(HBpz_3)_3$ was again observed. There is at least some precedence for the displacement of the cyclopentadienide moiety by the $HBpz_3^-$ ligand. Trofimenko[115] obtained $Fe(RBpz_3)_2$ in reactions of $RBpz_3^-$ with $(C_5H_5)Fe(CO)_2X$. Also King and Bond[131] obtained

$(CH_3)_3Pt(HBpz_3)$ from $KHBpz_3$ and $(CH_3)_3Pt(C_5H_5)$.

Because of difficulties experienced in isolating characterizable compounds the reaction of these $(HBpz_3)_nMCl_{3-n}$ complexes with organometallic reagents was abandoned.

5. Conclusion

We have demonstrated that poly(pyrazol-1-yl)borate complexes can be prepared with the lanthanide metals. The complexes obtained include the solid, air stable $M(HBpz_3)$, derivatives and the hygroscopic $(HBpz_3)_nMCl_{3-n}\cdot$ xTHF compounds.

The range of metals involved for the two series of compounds noted above parallels the behavior of the cyclopentadienide derivatives, i.e., the chloro derivatives appear to be limited to complexes with the later lanthanides and no limitation exists for the $M(HBpz_3)_3$ series.

This parallel behavior with the cyclopentadienide complexes,however, does not continue in all aspects of the chemistry of these complexes.

The Lewis acidic character of the $M(C_5H_5)_3$ complexes has been noted in the introduction and it is to be contrasted to the complete absence of such behavior in the $M(HBpz_3)_3$ complexes. Also, the air stability of the $M(HBpz_3)_3$ derivatives in the solid state is in marked contrast to the tricyclopentadienide complexes. An interesting feature discussed for the $M(HBpz_3)_3$ complexes is the existence of two solid state structural classes for compounds with early and late lanthanides. The exact nature of the changes between the early and late members of the series awaits X-ray crystallographic analysis of one of the early members.

The reactivity of the chloro compounds is also very different. The reaction of $K_2C_8H_8$ with $(HBpz_3)MCl_2$ did yield the "mixed sandwich" complexes, analogous to the $(C_5H_5)M(C_8H_8)$ complexes. However, in contrast to the $(C_5H_5)_2MR$, attempts to prepare σ-bonded hydrotris(pyrazol-1-yl)borate containing organolanthanides have met with great difficulties and the desired compounds could not be isolated.

CHAPTER SIX

SYNTHESIS OF $M(N^ipr_2)_3$ COMPLEXES

1. Introduction

The subject of metal dialkylamides was extensively reviewed by Bradley in 1972[132] and by Bradley and Chisholm in 1976.[133] The synthetic utility of this class of compounds is demonstrated by their ability to react with protic species and to undergo insertion reactions with unsaturated substrates. The metal dialkylamides are also of interest because the steric requirements of the ligands are capable of stabilizing unusually low coordination numbers.

Bradley *et al.*[134] made use of the bulky ligand, $[N(SiMe_3)_2]^-$, to prepare three coordinate lanthanide complexes, $M[N(SiMe_3)_2]_3$ (M = La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Y, Yb, Lu). The compounds are monomeric, sublime at 75-100°C and 10^{-4} mmHg, and are soluble in hydrocarbon solvents from which they could be crystallized. Their properties made the synthesis of tris(diisopropylamido)lanthanide(III) complexes attractive. It was felt that the use of the diisopropylamido ligand, $[N^ipr_2]^-$, may provide sufficient steric hindrance to isolate monomeric $M(N^ipr_2)_3$ (M = lanthanide metal) complexes and that these compounds would act as starting materials for the synthesis of other lanthanide complexes. In particular, neutral six coordinate molecules could potentially be synthesized by carrying out insertion reactions with unsaturated substrates such as CO_2, COS, and CS_2. This would provide the opportunity to extend and to study the chemistry of a relatively rare coordination number in lanthanide chemistry.

This chapter will describe the attempted preparation of $M(N^{i}pr_2)_3$ complexes, and the difficulties encountered in the syntheses. During the course of the work Bradley *et al.*[135] did report the synthesis of such compounds for M = Nd, Y, and Yb. However, the neodymium complex crystallized with one molecule of coordinated THF. This indicates that, at least with the larger Nd^{3+} ion, the size of the $N^{i}pr_2$ moiety is not sufficient to stabilize three coordination.

2. Results and Discussion

The preparative route for the synthesis of $M(N^{i}pr_2)_3$ complexes was identical to the method described by Bradley[134] for the synthesis of the corresponding silylamides. It involves the interaction of three equivalents of lithium diisopropylamide with anhydrous lanthanide chloride in THF solvent at room temperature. eq. (VI-1)

$$MCl_3 + 3LiN^{i}pr_2 \xrightarrow[R.T.]{THF} M(N^{i}pr_2)_3 + 3LiCl \qquad (VI\text{-}1)$$

M = Pr, Sm, Nd

In the Pr reaction, the contents of the flask were stirred overnight, and the color of the solution changed from green to light yellow-green and finally to brown during this time. The solvent was removed *in vacuo*, the residue was extracted with pentane and the LiCl was removed by filtration. Cooling the filtrate at -20°C produced light yellow crystals and a brown film on the bottom of the flask. The crystals were separated from the supernatant liquid and recrystallized from pentane. Again, light yellow crystals were obtained but there was also the brown film coating the bottom of the flask. Repeated recrystallization produced crystals that became yellow-brown in color and began to have a sticky surface which was difficult to dry. Repetition of the above procedure has allowed the initial isolation of crystals ranging in color from pale green to yellow-brown. However, in each case it was observed that recrystallization eventually led to yellow-brown sticky solids. A satisfactory analysis for $Pr(N^{i}pr_2)_3$ could not be obtained. Similar problems were encountered in the Sm and Nd reactions. With samarium only an oil product could be obtained. Crystallization from the red-brown pentane solution containing the original crude material could not be induced even when the solution was kept at -78°C overnight. Crystallization of the neodymium product was more successful, but instead of a single compound, a mixture of blue and green crystals was obtained. Attempts to separate the crystals were unsuccessful and recrystallization again yielded a sticky solid.

The difficulties experienced in the above reactions, especially the inability to purify the complexes by recrystallization, suggested that the complexes were either unstable or contained a mixture of compound or both.

The mass spectra of the solid products obtained from the various Pr and Nd preparations gave support for the formation of more than one complex. The spectra of the Pr compound, in addition to the expected parent ion at m/e 441, also contained ions at m/e 448, 548, 555 and 349. These ions correspond to $Li[Pr(N^ipr_2)_3]^+$, $Li[Pr(N^ipr_2)_4]^+$, $Li_2[Pr(N^ipr_2)_4]^+$, and $Li[Pr(N^ipr_2)-(HN^ipr_2)]^+$, respectively. Although absent from the spectra of the purest samples, see Experimental section, the presence of these ions in some spectra show that $LiPr(N^ipr_2)_4$ can also form and could complicate the isolation of pure $Pr(N^ipr_2)_3$. The mass spectrum obtained from the mixture of blue and green neodymium crystals also showed, in addition to $Nd(N^ipr_2)_3^+$, an ion corresponding to $Li[Nd(N^ipr_2)_3]^+$. However, the mass spectra of these complexes also indicated the presence of THF in the compounds. This is in line with the report of Bradley[135] which showed that the neodymium diisopropylamide is in fact the mono THF adduct, $Nd(N^ipr_2)_3 \cdot THF$.

It is quite likely that the pure Pr complex of this work also contains a molecule of THF.

In an effort to aid in the isolation of pure and solvent free amido complexes the Pr reaction was repeated in hexane and in benzene. However, in both cases only lightly colored solutions were obtained and some of the reactants remained undissolved. Filtration and evaporation of the filtrate followed by mass spectral investigation showed no evidence of complex formation. A mass spectrum of the solid filtered from the reaction flask also did not indicate $Pr(N^ipr_2)_3$.

At this point, being unable to purify satisfactorily the $M(N^ipr_2)_3$ complexes, it was hoped that, by reacting the complexes with an appropriate substrate, a more easily purifiable product could be obtained. In this way the goal of utilizing the $M(N^ipr_2)_3$ derivatives as reagents in lanthanide chemistry would be reached.

The most obvious choice of reagent is one that will produce a complex similar to already known derivatives. For this reason the insertion reaction with CS_2, eq. (VI-2), was carried out.

$$M(N^ipr_2)_3 + \text{excess } CS_2 \xrightarrow[\text{R.T.}]{C_6H_6} M(S_2CN^ipr_2)_3 \qquad \text{(VI-2)}$$

M = Pr, Nd, Sm

The reactions proceeded rapidly in each case. The appropriate dithiocarbamate complex precipitated from solution and was identified by mass spectrometry. Tris-(diethyldithiocarbamate) complexes have been reported by Brown *et al.*[136] The colors of the Pr, Nd, and Sm complexes are pale green, blue, and white respectively. The color of the complexes obtained in the present study are yellow-green for Pr and Nd and brown for Sm.

Although the mass spectra exhibit a simple fragmentation pattern, corresponding to the ions, $M(S_2CN^ipr_2)_3^+$, $[M(S_2CN^ipr_2)_3-CH_3]^+$, $M(S)(S_2N^ipr_2)^+$ and $M(S_2CN^ipr_2)_2^+$ because the color of the complexes are unexpectedly different from the diethyldithiocarbamate derivatives it is most probable that the compounds contain other nonvolatile component(s). There is no longer any indication of THF in the mass spectra. The $Pr(S_2CN^ipr_2)_3$ complex dissolved in CH_2Cl_2 to give a yellow-green solution. However, crystallization attempts failed and only brown oily residues were obtained. At this point further work with the amides was discontinued.

3. Conclusion

In retrospect it is clear that the major problem associated with the isolation of pure tris(diisopropylamido)lanthanide(III) complexes in this study does not reside in the formation of mixtures. Although $Li[M(N^ipr_2)_4]$

compounds have been seen in some of the preparations, solid materials whose mass spectra showed only $M(N^{i}pr_{2})_{3}$ have been obtained also. The report of Bradley *et al.*[135] also indicates that pure $M(N^{i}pr_{2})_{3}$ complexes can be isolated and characterized. However, these authors showed that the molecules are thermally unstable and whereas tricoordinate compounds are obtained in good yield with Y and Yb, the Nd complex forms a four coordinate THF adduct only in low yields.[135b] The presence of THF also has been established in the compounds of this study.

It is thus probable that the difficulties experienced with our compounds are related to thermal instability, and the presence of the THF molecule. The repeated crystallization and drying, in our attempts to purify the complexes, probably have resulted in some loss of coordinated THF which rendered the compounds more prone toward decomposition. The initially well formed crystals with Pr and Nd which deteriorate to sticky solids upon recrystallization is consistent with this suggestion.

Thus, even though pure lanthanide diisopropylamides can be synthesized, their utility as starting materials for the preparation of other lanthanide complexes is severly limited by their delicate nature and by the problems associated with their isolation.

CHAPTER SEVEN

EXPERIMENTAL PROCEDURES

1. General

The handling of these very air-sensitive organolanthanide complexes was performed under an atmosphere of purified nitrogen. High purity nitrogen was passed through a heated column of BASF catalyst Re-11 to remove oxygen and then through a column of Aquasorb (Mallinkrodt) to remove traces of water prior to entering a double manifold. All manipulations of the compounds were accomplished with the aid of the double manifold (vacuum/nitrogen); standard Schlenk techniques[137] were employed.

Solvents

Solvents were purified according to standard procedures[137] with all operations performed under purified nitrogen unless otherwise stated. Reagent grade solvents were used.

Tetrahydrofuran was refluxed over lithium aluminum hydride for 18-20 hours and then distilled onto sodium/potassium alloy. After refluxing an additional 10-12 hours, benzophenone was added. Once the blue color of the benzophenone ketyl radical developed and persisted the solvent was suitable for use. The tetrahydrofuran was then freshly distilled just prior to use and transferred by syringe. Syringe transfer technique was used with all solvents. Benzene and toluene were refluxed over potassium initially for 8-10 hours and kept in contact with the metal. They were then distilled as needed. Hexane and pentane, commercial grade, were washed with sulfuric acid until no color developed in the acid layer. The solvents were washed with water, aqueous sodium hydroxide and water again. After drying over magnesium sulfate (these operations not under nitrogen) hexane was transferred onto sodium/potassium alloy and pentane onto calcium hydride. After an initial reflux period of ~18 hours the solvents were distilled as needed. Before using pentane it was necessary to first degass the solvent by repeated freeze-evacuate-thaw cycles. Pyridine was refluxed over and distilled from barium oxide. It was then freeze-thaw degassed.

Spectral Analyses

Infrared spectra of the compounds were recorded on a Perkin-Elmer Model 467 spectrophotometer as mineral oil or halocarbon oil mulls sandwiched between KBr discs. The mineral oil was distilled from sodium and the halocarbon oil was stored over Linde 4A molecular sieves. All organolanthanide samples were prepared in a nitrogen filled glove bag.

Raman spectra were recorded on solid samples sealed in capillaries under nitrogen using a Beckman 700 Raman laser spectrophotometer equipped with an Ar-laser.

Mass spectra were recorded on solid samples with an AEI MS-12 spectrometer operating at 70 eV unless otherwise stated. The samples were introduced into the spectrometer by a direct probe technique. A sealed, nitrogen filled capillary containing the complex was broken immediately before insertion into the vacuum chamber. In this manner mass spectra of the very air-sensitive organolanthanide complexes were obtained.

Proton magnetic resonance spectra were recorded on several instruments: Varian A-60 or A-56/60, Perkin-Elmer R32 operating at 90 MHz, and Varian HA-100 interfaced to a Digilab FTS/NMR-3 data system. Carbon-13 spectra were recorded on a Bruker HFX-90 (22.6 MHz), a Bruker WP-60 (15.08 MHz) and a Bruker WH-400 (100.6 MHz). The deuterated solvents for NMR work were freeze-thaw degassed. Pyridine-d_5 and DMSO-d_6 were dried over barium oxide and vacuum distilled onto Linde 4A molecular sieves. Benzene-d_6 and toluene-d_8 were distilled from potassium and stored over molecular sieves. Methylene chloride-d_2 was distilled from phosphorus pentoxide and stored over molecular sieves. Solutions of the complexes were then introduced to dry, nitrogen filled NMR tubes. The NMR tubes were either equipped with a serum cap through which the solution was introduced with a syringe or they were attached to a filling adapter[138] comprised of a constricted 14/20 ground glass joint and stopcock that could be attached to the double manifold *via* vacuum tubing. This permitted sealing the NMR samples *in vacuo*. Chemical shifts are referenced to the residual protons giving rise to solvent peaks and converted to TMS values.

Electronic spectra were recorded on Cary 14 or Unicam SP 1700 spectrophotometers. The top of a 1-cm quartz cell was fitted with a serum cap which enabled filling of the cell with dry nitrogen after evacuation. Solutions of the complexes were then introduced to the cell *via* syringe and the spectra recorded immediately. The spectra were usually recorded several times using different solutions and concentrations, the molar extinction coefficient remained constant to within 15%.

Elemental Analysis

Elemental analysis of the mixed sandwich complexes has proved to be very difficult due to the extreme air sensitivity of the compounds. Similar difficulties have been encountered by a number of researchers,[11,14,49] in their attempts to obtain analyses for other organolanthanide derivatives. Nevertheless, analyses were attempted at the Alfred Bernhardt Microanalytical Laboratory, West Germany and Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Samples sealed *in vacuo* were sent to these two companies but met with varied success. This, in most instances, is attributed to the difficulty in handling the complexes, which is particularly true for the powdery, unsolvated mixed sandwich complexes. The analyses done at these commercial laboratories for a small representative number of complexes substantiates the formulation of the mixed sandwich derivatives and base adducts. The combination of elemental analyses, NMR spectroscopic data, and mass spectral data further supports the formulation of the mixed sandwich complexes and the Lewis base adducts in this study.

The carbon, hydrogen, and nitrogen combustion analyses for the lanthanide poly(pyrazol-1-yl)borate complexes were carried out in the microanalytical laboratory of this university.

2. Synthesis of the Mixed Sandwich Complexes, $(C_5H_5)M(C_8H_8)$ base adducts and reactivity.

Starting materials

MCl_3 (M = lanthanide metal)

Anhydrous lanthanide chlorides were prepared from the hydrated salt (Research Chemicals, Phoenix or Rare Earth Division, American Potash and Chemical Corp., West Chicago) using thionyl chloride (Aldrich Chemical Co.,) as described by Freeman and Smith.[139] An example follows:

A 200 ml nitrogen filled flask was charged with 19.2 g (0.05 mole) of finely ground $SmCl_3 \cdot 6H_2O$. To the flask was added 60 ml (0.8 mole) of freshly distilled thionyl chloride. The initial exothermic reaction is allowed to subside and the contents of the flask are then stirred and refluxed for 15 hours. The mixture is allowed to cool to room temperature and the solid to settle to the bottom of the flask. The supernatant liquid is then removed with a syringe and another 60 ml (0.8 mole) of $SOCl_2$ is added to the flask. The mixture is refluxed for 10 hours and after cooling, the $SOCl_2$ is removed with a syringe. The $SmCl_3$ is washed with 50 ml portions of dry benzene until no further color develops in the solvent layer. After filtering the last benzene washing the anhydrous $SmCl_3$ is dried under vacuum at room temperature for 36 hours.

$\underline{NaC_5H_5}$

Cyclopentadiene was obtained by heating the dimer (Eastman Organic Chemicals) at ca. 110°C under nitrogen, and the monomer (b.p. = 42.5°C) was collected in a flask maintained at -78°C. It was then reacted with sodium sand in the usual manner to produce sodium cyclopentadienide.

$\underline{K_2C_8H_8}$

Cyclooctatetetraene (BASF) was freeze-thaw degassed and vacuum distilled onto Linde 4A molecular sieves.

It was then converted to the dianion by a procedure similar to that of Katz *et al.*[140]

To a 1 liter 3-neck flask equipped with a mechanical stirrer and dropping funnel was added THF (230 ml). The solvent was cooled to -40°C and 7.95 g (0.2 mole) of potassium, freshly cut in small pieces to expose a clean metallic surface, was added. The dropping funnel was charged with 10 ml of THF and 9.4 ml of cycloctatetetraene (0.083 mole). The cycloctatetetraene was then slowly added to the rapidly stirred potassium and the temperature of the flask was kept at ca. -40°C overnight. The dropping funnel was then rinsed with 10 ml of THF and the yellow-brown solution was kept stirring at -30°C for an additional 8 hours. The contents of the flask were then filtered to remove the excess potassium metal. The concentration of the solution (0.36 M) was determined by hydrolysis of the $K_2C_8H_8$ under nitrogen followed by titration of the resulting potassium hydroxide with hydrochloric acid. This stock solution must be used within 2-3 days to avoid decomposition of the very air sensitive $K_2C_8H_8$.

$[C_8H_8MCl\cdot 2THF]_2$

The monocyclooctatetraenide complexes of the early lanthanides were prepared and isolated according to the procedure of Streitwieser *et al.*[11]

$(C_5H_5)MCl_2 \cdot 3THF$

The monocyclopentadienide derivatives for the heavy lanthanides were synthesized according to the method of Dubeck *et al.*[17] The melting points of the crystallized complexes were compared to the literature values. Although the complexes reported by Dubeck *et al.* had satisfactory elemental analyses a recent ^1H NMR spectrum of the lutetium complex recorded in these laboratories in pyridine-d_5 appears to indicate the presence of four THF molecules per lutetium (δ6.32, 5H, C_5H_5; δ3.65, 16.2H, THF; δ1.66, 15.9H, THF). The spectrum is shown in Figure 17. In all previous reactions with the monocyclopentadienide lanthanide complexes the formulation according to Dubeck had been assumed. The reason for this "extra" THF molecule in the lutetium complex has not yet been identified.

Other reagents

Cyclohexylisocyanide (Aldrich) was degassed, vacuum distilled onto and stored over Linde 4A molecular sieves.

Anhydrous 1,10-phenanthroline (Aldrich) and anhydrous iron(II)iodide (Alfa Inorganics) were used without further purification. Trimethyl chlorosilane (Silar Laboratories Inc., Watervliet, N.Y.), mercury(II)chloride, and ytterbium metal (Rare Earth Division, American Potash and Chemical Corp.) were used as received. Ammonia was condensed from

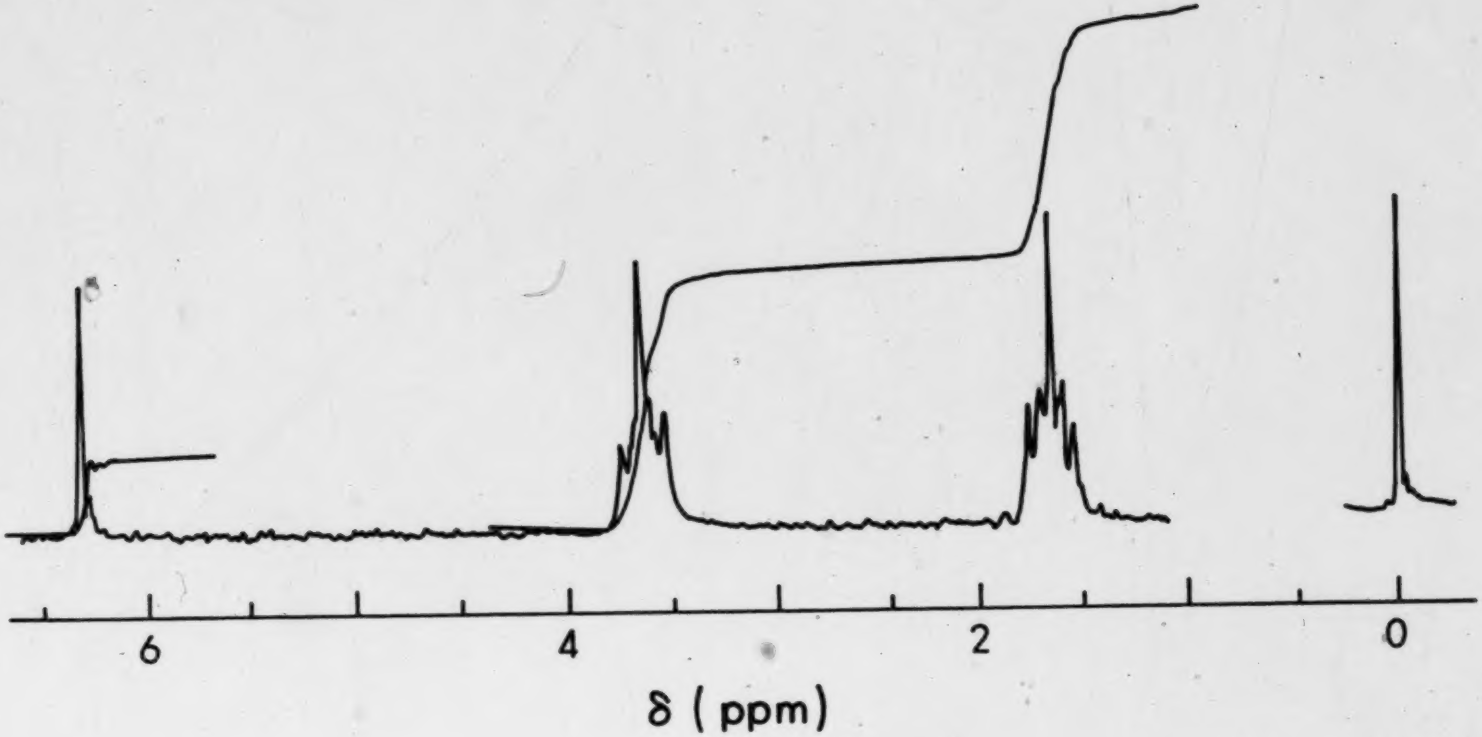

Figure 17. ^{1}H NMR spectrum of $(C_5H_5)LuCl_2 \cdot 4THF$ in pyridine-d_5.

a lecture bottle onto sodium metal and allowed to stir at reflux for 30 minutes. It was then distilled into the reaction vessel.

$(C_5H_5)M(C_8H_8)\cdot THF$ and $(C_5H_5)M(C_8H_8)$

The synthesis of several lanthanide mixed sandwich THF adducts will be described since these complexes served as starting materials in subsequent preparations. The syntheses described will also illustrate the general preparative method involved and the experimental difficulties encountered in obtaining pure products. In addition, some physical data which helped in securing the composition of the complexes will be given.

M=Ho

To a rapidly stirred solution of $(C_5H_5)HoCl_2\cdot 3THF$ (1.47 g, 2.85 mmol) in THF (50 ml) at -30°C was added slowly a 0.256 M THF solution of $K_2C_8H_8$ (11.1 ml, 2.85 mmol). The reaction mixture was maintained at -30°C for 1 hour and then allowed to warm slowly to room temperature. After a total reaction time of 18 hours the volume of the yellow solution was reduced to 30 ml by evaporation at reduced pressure and filtered to remove KCl. To the yellow filtrate was added 10 ml of hexane followed by cooling at -20°C for 36 hours to produce bright yellow crystals of $(C_5H_5)Ho(C_8H_8)\cdot THF$. The compound was recrystallized from a minimum of THF/hexane solvent mixture until judged free of chloride ion by $AgNO_3$ test to give

0.50 g (43% yield) of pure compound. The mass spectrum of the complex is listed in Table 28 and the infrared spectrum in Table 29.

The coordinated THF molecule was then quantiatively removed by vacuum drying at 10^{-3} mmHg/50°C for 1.5 hours. Anal. Calcd for $C_{13}H_{13}Ho$: C, 46.73; H, 3.92; Ho, 49.35. Found: C, 46.13; H, 4.02; Ho, 49.65.

M=Er

The THF adduct of the erbium complex was prepared and isolated exactly as the holmium analogue. Yield 48%. Anal. Calcd for $C_{17}H_{21}ErO$: C, 49.97; H, 5.18; Er, 40.93; O, 3.92. Found: C, 49.81; H, 5.07; Er, 41.53; O, 3.98. The THF was then removed by vacuum drying 10^{-3} mm Hg/50°C until no evidence for THF appeared in the mass spectrum.

M=Yb

To a rapidly stirred solution of $(C_5H_5)YbCl_2 \cdot 3THF$ (3.47 g, 6.6 mmol) in THF (50 ml) at -50°C was added slowly a 0.258 M THF solution of $K_2C_8H_8$ (25.6 ml, 6.6 mmol). The initially orange solution underwent color changes to bluish-green after the first 1-2 ml of $K_2C_8H_8$ were added and then the blue coloration continued to increase in intensity as addition was completed over a 1 hour period. The contents of the flask were kept at ca. -40°C for an additional hour and then allowed to

Table 28. Relative Abundance (%) of Fragment Ions in the Mass Spectrum of $(C_5H_5)M(C_8H_8)\cdot THF$

Ion	M = Ho	M = Nd
$C_{13}H_{13}M^+$	100	40
$C_{11}H_{11}M^+$	4	<1
$C_8H_8M^+$	49	89
$C_8H_6M^+$	21	-
$C_7H_6M^+$	7	3
$C_5H_5M^+$	55	100
C_2HM^+	10	13
$C_{13}H_{13}M^{2+}$	3	3
M^+	24	20
$C_{11}H_{11}M^{2+}$	6	3
$C_8H_8{}^+$	14	7
$C_7H_7{}^+$	7	10
$C_6H_6{}^+$	25	20
$C_4H_8O^+$	36	180
$C_4H_7O^+$	32	160
$C_5H_6{}^+$	25	56
$C_5H_5{}^+$	13	37
$C_4H_4{}^+, C_8H_8{}^{2+}$	5	6
$C_4H_3{}^+$	9	10
$C_3H_6{}^+$	66	500

Table 29. Infrared spectra of $(C_5H_5)M(C_8H_8)\cdot$THF Complexes.[a]

M = Ho	M = Nd
1438m	1436w-m
1339w	1342w
1308vw	1310vw
1261w	1253w
1171vw	1178vw
1058vw	
1030s	1023s
1012s	1010s
918w	926w
897m-s	897m
880s	870s
	799w
798s	778s
781s	768s
751sh	756w
746sh	
714s	704s
697s	695s
671sh	677w
647vw	652vw

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[a] Frequencies in cm^{-1}; abbreviations as in Table .

warm slowly to room temperature overnight. The reaction mixture was filtered to remove the precipitated KCl and a blue insoluble complex which was later identified as $Yb_2(C_8H_8)_3$. The blue filtrate was cooled to -20°C for 4 hours producing more $Yb_2(C_8H_8)_3$, collected by filtration, and a small amount of the desired $(C_5H_5)Yb(C_8H_8)\cdot THF$ as indicated by infrared and mass spectral analysis. The final blue filtrate was kept at -20°C until crystallization was complete to give 1.30 g (47% yield) of pure $(C_5H_5)Yb(C_8H_8)\cdot THF$. Anal. Calcd for $C_{17}H_{21}OYb$: C, 49.27; H, 5.11; Yb, 41.76. Found: C, 48.91; H, 4.88; Yb, 42.25.

M=Y

Two methods were employed for the preparation of the yttrium complex. The first method, (i), is based on an *in situ* preparation of $(C_8H_8)YCl$ and is only suitable for the synthesis of the unsolvated complex. The second route, (ii), consists of the prior isolation of $(C_5H_5)YCl_2$ and its subsequent reaction with $K_2C_8H_8$, the conventional method described before for M = Ho, Er, Yb. The latter synthesis is suitable for both THF adduct and unsolvated complex.

(i) To a rapidly stirred slurry of anhydrous YCl_3 (9.6 g, 0.05 mol) in 60 ml of THF at ca. -50°C was added dropwise a 0.26 M THF solution of $K_2C_8H_8$ (192 ml, 0.05 mol).

After addition was complete the yellow-brown solution was allowed to warm to room temperature overnight. At this point the color of the solution is bright yellow. The contents of the flask were then cooled again to -40°C and 4.35 g (0.05 mol) of NaC_5H_5 in 40 ml of tetrahydrofuran was slowly added to the reaction mixture. This produced a reddish-yellow color after warming to room temperature overnight. The solvent was then removed from the flask *in vacuo* and the resulting orange residue was transferred to an apparatus suitable for sublimation in a tube furnace. Colorless crystals of $(C_5H_5)Y(C_8H_8)$ were sublimed from the crude product at 100°C/10^{-3} mmHg. Yield 1.4 g (11%). ^1H NMR (toluene-d_8) δ6.25 (s, 8H); δ5.34 (s, 5H).

ii) In a manner similar to the preparation of the Ho and Er analogues, yellow crystals of $(C_5H_5)Y(C_8H_8)\cdot THF$ in approximately 35% yield were isolated. Anal. Calcd for $C_{17}H_{21}OY$: C, 61.83; H, 6.41; O, 4.84; Y, 26.92. Found: C, 61.57; H, 6.23; O, 5.11; Y, 26.77.

M=Lu

The yellow lutetium analogue was also prepared by a route analogous to the Ho and Er complexes in a yield of 43%. ^1H NMR (pyridine-d_5): δ6.20 (s, 8H), δ5.48 (s, 5H); δ3.59 (m, 4H); δ1.54 (m, 4H). The THF of solvation was then removed during sublimation at 115°C/10^{-4} mmHg giving colorless $(C_5H_5)Lu(C_8H_8)$. ^{1}H NMR (toluene-d_8): δ6.24 (s, 8H); δ5.29 (s, 5H).

M=Sm

The preparation of the samarium mixed sandwich complex was first attempted by procedure (i) above for the yttrium complex, but substituting crystallization for sublimation as the isolation method. This produced a mixture of a brown and a violet colored product which proved virtually inseparable by repeated crystallization from THF/hexane mixtures. The following procedure was more successful.

To a rapidly stirred solution of $(C_5H_5)SmCl_2 \cdot 3THF$ (1.8 g, 3.6 mmol) in THF (70 ml) at -20°C was added slowly a 0.4 M THF solution of $K_2C_8H_8$ (9 ml, 3.6 mmol). This immediately produced a violet solution. The contents of the flask were allowed to warm slowly to room temperature with rapid stirring. After a total reaction time of 15 hours the contents of the flask were filtered and the filtrate cooled to -20°C. Violet, extremely air-sensitive crystals were obtained. Mass spectral analysis indicated the presence of $Sm(C_5H_5)_3$ which necessitated repeated crystallization from THF/hexane mixtures to remove the undesired complex. This contributed to the low yield, 80 mg (6%). ^{1}H NMR (DMSO-d_6): δ7.48 (s, 8H); δ5.98 (s, 5H); δ3.68 (m, 4H); δ1.72 (m, 4H).

M=Nd

To a rapidly stirred slurry of $[(C_8H_8)NdCl\cdot 2THF]_2$ (0.43 g, 0.5 mmol) in 25 ml of THF cooled to -40°C was added a solution of NaC_5H_5 (0.12 g, 1.0 mmol) in 10 ml of THF over a period of 30 minutes. The reaction flask was kept at -40°C for one hour and then allowed to warm slowly to room temperature overnight. The contents of the flask were then filtered to remove precipitated NaCl which was contaminated with $Nd(C_5H_5)_3$ and possibly $Nd_2(C_8H_8)_3$ and the volume of the green filtrate was reduced to about 20 ml. Hexane (5 ml) was then added and cooling to -20°C produced bright green crystals which were isolated by filtration. Recrystallization from a minimum of THF/hexane solvent mixture gave 0.1 g (27% yield). The mass spectrum for the complex is listed in Table 28. ^1H NMR (pyridine-d_5): δ0.87 (s, 8H); δ2.79 (s, 5H); δ3.65 (m, 4H); δ1.62 (m, 4H). The coordinated THF was then removed by heating at 80°C/10^{-3} mm-Hg for *ca*. 2 hours.

M=Pr

The praseodymium complex was prepared in a similar way to give the pale green crystalline THF adduct in 20% yield.

$(C_5H_5)M(C_8H_8)\cdot L$

The adducts were obtained by direct reaction of the base with either the mixed sandwich complex or their

THF adducts. The compounds were then isolated as powders or crystalline products in near quantitative yield usually by the addition of hexane to the reaction mixture. Two example will describe the general preparative scheme.

M=Ho, L=$C_6H_{11}NC$

To a slurry of $(C_5H_5)Ho(C_8H_8)$ (0.27 g, 0.82 mmol) in 35 ml of toluene at 0°C was added an excess of $C_6H_{11}NC$ (0.3 ml, 2.5 mmol). The reaction flask was kept at 0°C for 4.5 hours during which time a clear golden-yellow solution was obtained. The volume of the solution was reduced to 15 ml and hexane (25 ml) was added. Cooling at -20°C for 12 hours produced long golden needles. The solvent was decanted and the golden needles were then washed with pentane and dried in a stream of nitrogen. Yield, 0.25 g (70%). Further addition of hexane to the supernatant solution and cooling produces only microcyrstalline product. The mass spectrum of the $(C_5H_5)Ho(C_8H_8)\cdot C_6H_{11}NC$ exhibits ions at m/e 443 $(P)^+$ and 334 $(P-C_6H_{11}NC)^+$.

M=Lu, L=$C_6H_{11}NC$

To a slurry of $(C_5H_5)Lu(C_8H_8)\cdot THF$ (0.05 g, 0.12 mmol) in 10 ml of toluene at room temperature was added $C_6H_{11}NC$ (0.015 ml, 0.12 mmol) diluted with 2 ml of toluene. After stirring at room temperature for 10 hours a clear yellow solution was obtained. The volume of solution was then reduced *in vacuo* to ca. 2 ml producing a slurry of the complex which was further dried by passing a stream of nitrogen through the flask. ^{1}H NMR (toluene-d_8): δ6.19 (s,8H); δ5.48 (s,5H); δ2.23 (m, 1.3H); δ0.91 (m, 13H). Infrared spectrum of the yellow solid shows ν(N-C) at 2197 cm^{-1}.

The colors of mixed sandwich complexes are collected in Table 30.

Bases that did not yield solid adducts

An example follows which typifies the procedure used with the bases noted in Chapter III that did not yield solid adducts.

To a rapidly stirred slurry of $(C_5H_5)Ho(C_8H_8)$ (0.33 g, 0.99 mmol) in 40 ml of toluene at 0°C was added NEt_3 (0.3 ml, 2.2 mmol). The contents of the flask were allowed to come to room temperature slowly and stirring was continued overnight. The volume of the yellow solution was reduced to ca. 25 ml and hexane was added until a faint cloudiness resulted. Cooling at -20°C produced yellow crystals. The supernatant was removed with a syringe and the crystals were washed with hexane. They were then dried in a stream of nitrogen. The infrared spectrum of the yellow solid contained no other absorption bands than those due to $(C_5H_5)Ho(C_8H_8)$. Adding hexane to the supernatant resulted in the isolation of

Table 30. Colors of the $(C_5H_5)M(C_8H_8)\cdot L$ Complexes and yields of the THF adducts.

M	Yield(%)	THF	-	$C_6H_{11}NC$	Py	NH_3	1,10-Phen
Pr	20	pale green		pale green			green
Nd	27	green	blue-green		green	blue	
Sm	6	violet	metallic gray	purple	purple		
Y	35	yellow	colorless	yellow	yellow		
Ho	43	yellow	yellow	gold	yellow	yellow	maroon
Er	48	pink-orange	pink	orange			
Yb	47	blue		green			
Lu	43	yellow	colorless	yellow			

more $(C_5H_5)Ho(C_8H_8)$.

Reaction of $(C_5H_5)Ho(C_8H_8)$ with $HgCl_2$

To a solution of $(C_5H_5)Ho(C_8H_8)\cdot THF$ (0.082 g, 0.2 mmol) in 20 ml of THF was added $HgCl_2$ (0.027 g, 0.1 mmol) dissolved in THF (10 ml) at room temperature. The addition funnel and reaction flask were protected from the light using aluminum foil. The yellow THF solution developed a cloudiness as the $HgCl_2$ was added and within five minutes mercury metal was deposited.

Reaction of $(C_5H_5)Y(C_8H_8)$ with UCl_4

To a bright yellow solution of $(C_5H_5)Y(C_8H_8)\cdot THF$ (0.52 g, 1.56 mmol) in 25 ml of THF was added at 0°C a THF solution of anhydrous UCl_4 (0.296 g, 0.78 mmol).[141] This immediately produced a color change to a deep green-brown. An aliquot was removed and its UV-visible spectrum was recorded. By comparison to the literature data,[35b] the spectrum indicated that uranocene has been produced. After stirring the solution overnight at room temperature the solvent was removed *in vacuo* and sublimation gave uranocene which was further identified by its mass, ^1H NMR and infrared spectra.

Reaction of $(C_5H_5)Ho(C_8H_8)$ with FeI_2

To a solution of $(C_5H_5)Ho(C_8H_8)\cdot THF$ (0.156 g, 0.385 mmol) in 20 ml of THF at room temperature was added a solution of iron(II)iodide (0.059 g, 0.192 mmol) in

THF. After stirring for 4 hours at room temperature the solvent was removed *in vacuo* and sublimation at 50°C/10^{-3} mmHg gave orange crystals. Ferrocene was identified by its NMR in CS_2 and mass spectra.

Reaction of $(C_5H_5)Y(C_8H_8)$ with Me_3SiCl

Freshly sublimed $(C_5H_5)Y(C_8H_8)$ (0.0377 g, 0.146 mmole) was dissolved in 0.5 to 0.6 ml of pyridine-d_5 giving a deep yellow solution. It was transferred to a serum stoppered NMR tube and increments of degassed Me_3SiCl were added using a 50 µl syringe (see Chapter III). The NMR tube was shaken for 10-15 minutes at room temperature followed by the recording of the NMR spectrum. Successive addition of 0.011 ml (0.086 mmol), 0.011 ml, 0.019 ml (0.149 mmol), and 0.029 ml (0.227 mmol) were made.

Reaction of $(C_5H_5)Er(C_8H_8)$ with Me_3SiCl

To a solution of $(C_5H_5)Er(C_8H_8)$ (0.23 g, 0.65 mmol) in 25 ml of THF was added Me_3SiCl (0.017 ml, 1.3 mmol) diluted with 5 ml of THF. The reaction was started at 0°C and then allowed to warm to room temperature overnight. A very small amount of pale orange precipitate was observed which was removed by filtration. The solvent was removed from the filtrate *in vacuo* and the mass spectrum of the crude reaction mixture indicated $C_8H_8(SiMe_3)_2$ as the only volatile product. The crude product was extracted with ether, the mixture filtered and after removing the ether, sublimation at 50°C/10^{-3} mmHg produced a white solid. The ^{1}H NMR spectrum of this material in $CDCl_3$ was in agreement with the literature data for $C_8H_8(SiMe_3)_2$.[111]

3. Synthesis of the Dinuclear Compounds, $M_2(C_8H_8)_3$.

To a rapidly stirred slurry of $YbCl_3$ (1.86 g, 6.65 mmol) in 45 ml of THF at -40°C was added a 0.266 M THF solution of $K_2C_8H_8$ (37.5 ml, 9.98 mmol). At the start of the addition of the dianion the temperature of the cold bath was lowered to -60°C. Immediately the reaction mixture became deep blue. The cold bath around the reaction flask was kept at -60°C for 4 hours after addition was complete. The flask was then allowed to warm slowly to room temperature overnight. The contents of the flask were filtered leaving a mixture of KCl and $Yb_2(C_8H_8)_3$ on the filter frit. The deep blue filtrate was cooled at -20°C to yield deep blue crystals of $Yb_2(C_8H_8)_3$. The crystals gave negative chloride and potassium (flame) ion tests. The complex has identical (see Chapter IV) properties to the by-product $Yb_2(C_8H_8)_3$, obtained in the $(C_5H_5)Yb(C_8H_8)$ synthesis, for which Anal. Calcd for $C_{24}H_{24}Yb_2$: C, 43.77; H, 3.67; Yb, 52.55. Found: C, 43.52; H, 3.48; Yb, 51.96.

The yellow $Lu_2(C_8H_8)_3$ was isolated as the by-product from the $(C_5H_5)Lu(C_8H_8)$ preparation. Anal. Calcd for

$C_{24}H_{24}Lu_2$: C, 43.52; H, 3.65; Lu, 52.83. Found: C, 42.80; H, 3.44; Lu, 53.20. Mol. wt. by osmometry in pyridine Calcd: 662. Found: 308.

$Yb(C_8H_8)$

The red to red-purple $Yb(C_8H_8)$ complex was prepared according to the method of Hayes and Thomas.[26] The compound was obtained as a powder from a pyridine/hexane solvent mixture. The solvated pyridine was removed at 110°C/10^{-3} mmHg producing the same red complex. Anal. Calcd for C_8H_8Yb: C, 34.66; H, 2.91; Yb, 62.42. Found: C, 34.67; H, 2.96; Yb, 62.36.

4. Hydrotris(pyrazol-1-yl)borate syntheses

Starting Materials

The $KHBpz_3$ compound was synthesized by the procedure of Trofimenko.[118]

LiMe and $C_6H_5CH_2MgCl$ were obtained from Alfa-Ventron Corp. and were standardized by the acidometric double titration method[142] or by the procedure of Watson and Eastham[143] employing s-butanol as titrant and 1,10-phenantholine as a color indicator. Literature preparations were used to obtain $Mg(CH_2SiMe_3)_2$[144] and o-lithio-p-tert-butyl-N,N-dimethylbenzylamine.[145]

$M(HBpz_3)_3$

M=Pr

To $PrCl_3 \cdot 7H_2O$ (0.29 g, 0.78 mmol) was added 20 ml of distilled water. The solution was filtered to remove a very small amount of undissolved material. The clear solution of $PrCl_3$ was added at a rapid drop rate to a stirred aqueous solution (20 ml) of $KHBpz_3$ (0.58 g, 2.3 mmol). A pale green precipitate formed immediately. Stirring was continued for 10 minutes and then the product was isolated by filtration. The pale green solid was washed with two 10 ml portions of water and then air dried. Yield; 0.58 g, 95%. Anal. Calcd for $C_{27}H_{30}B_3N_{18}Pr$: C, 41.58; H, 3.88; N, 32.32. Found: C, 41.11; H, 3.83; N, 31.74.

The La and Sm complexes were prepared similarly. See Table 31 for the color, yield, and analytical data.

M=Er

To $ErCl_3 \cdot 6H_2O$ (0.36 g, 0.94 mmol) was added 12 ml of H_2O and the solution filtered to remove a small amount of undissolved material. The clear solution of $ErCl_3$ was rapidly added to a stirred aqueous solution (15 ml) of $KHBpz_3$ (0.71 g, 2.8 mmol). A pink precipitate formed immediately. The slurry was stirred for 10 minutes at room temperature and filtered. The pink solid was washed with two 10 ml protions of water and the complex air dried. The $Er(HBpz_3)_3$ was then crystallized from toluene. Yield; 0.65 g, 86%. Anal. Calcd for $C_{27}H_{30}B_3N_{18}Er$: C, 40.22; H, 3.75; N, 31.27. Found: C, 40.43; H, 3.83;

Table 31. Color, yield, and analysis for $M(HBpz_3)_3$ Complexes.

			Analysis					
			Calcd.			Found		
M	Color	Yield, %	C	H	N	C	H	N
La	Colorless	95	41.68	3.89	32.41	41.02	3.88	32.37
Pr	Pale green	95	41.58	3.88	32.32	41.11	3.83	31.74
Sm	Colorless	94	41.08	3.77	31.94	40.95	3.77	31.94
Y	Colorless	80	44.55	4.15	34.63	45.96	4.35	33.61
Er	Pink	86	40.22	3.75	31.27	40.43	3.83	30.66

N, 30.66. Molecular weight by osmometry in C_6H_6: Calcd 806; Found 799.

The yttrium analogue was prepared in a similar manner.

All subsequent reactions were carried out under an inert atmosphere.

$(HBpz_3)ErCl_2 \cdot 1.5THF$

To a rapidly stirred slurry of $ErCl_3$ (1.42 g, 5.1 mmol) in 55 ml of dry THF at room temperature was added a solution of $KHBpz_3$ (1.3 g, 5.1 mmol) in 45 ml of THF. Stirring was continued overnight at room temperature. Precipitated KCl was removed by filtration. The volume of the pink filtrate was reduced to ca. 25 ml and 5 ml of dry hexane was added. Upon cooling at -20°C, light pink crystals were obtained. Yield; 1.45 g, 58%. Anal Calcd for $C_{15}H_{22}BCl_2N_6O_{1.5}Er$: C, 32.21; H, 3.96; N; 15.02. Found: C, 32.67; H, 3.96; N, 14.76.

$(HBpz_3)_2ErCl \cdot THF$

To a rapidly stirred slurry of $ErCl_3$ (0.70 g, 2.5 mmol) in 45 ml of dry THF at room temperature was added a solution of $KHBpz_3$ (1.28 g, 5 mmol) in 30 ml of THF. The reaction mixture was stirred at room temperature overnight and filtered to remove KCl. The pink filtrate was concentrated until a faint cloudiness appeared and then cooled at -20°C producing a light pink powder. The complex was separated by filtration and vacuum dried.

Yield; 1.0 g, 57%. Anal. Calcd for $C_{22}H_{28}B_2ClErN_{12}O$: C, 37.70; H, 4.03; Cl, 5.06; N, 23.98. Found: C, 37.51; H, 4.29; Cl, 5.22; N, 24.04.

The yttrium derivative was prepared in a similar manner with a yield of 60%. Anal. Calcd for $C_{22}H_{28}B_2ClN_{12}OY$: C, 42.45; H, 4.53; N, 27.00. Found: C, 41.68; H, 4.44; N, 28.74.

$(HBpz_3)Er(C_8H_8)$

To a rapidly stirred solution of $(HBpz_3)ErCl_2 \cdot 1.5THF$ (0.78 g, 1.4 mmol) in 30 ml of THF at -50°C was added slowly a 0.266 M solution of $K_2C_8H_8$ (5.3 ml, 1.4 mmol). The contents of the flask were kept at ca. -30°C for one hour after addition was complete and then allowed to warm slowly to room temperature overnight. Precipitated KCl was removed by filtration. Hexane (5 ml) was added to the reddish-pink filtrate. Cooling at -20°C produced pink crystals of $(HBpz_3)Er(C_8H_8)$. These were separated by filtration and washed with hexane. Yield; 0.38 g, 56%. Anal. Calcd for $C_{17}H_{18}BN_6Er$: C, 42.15; H, 3.75; Er, 34.53; N, 17.35. Found: C, 43.33; H, 3.71; Er, 33.91; N, 16.78.

The lutetium derivative was prepared similarly and purity ascertained by ^1H NMR spectroscopy.

Reaction of $(HBpz_3)_2YCl\cdot THF$ with o-lithio-p-tert-butyl-N,N-dimethylbenzylamine.

To a rapidly stirred slurry of $(HBpz_3)_2YCl\cdot THF$ (0.46 g, 0.74 mmol) in 30 ml of toluene was added a slurry of o-lithio-p-tert-butyl-N,N-dimethylbenzylamine (0.15 g, 0.74 mmol) in 10 ml of toluene at room temperature. The reaction mixture was stirred overnight at room temperature producing a light yellow solution and a small amount of off-white precipitate. The precipitate was removed by filtration and the volume of the clear light yellow filtrate was concentrated to ca. 20 ml. Hexane was added until there appeared to be a faint cloudiness and the contents of the flask were cooled to -50°C. Crystallization could not be induced. The solvent was then removed *in vacuo* giving a light yellow solid. A mass spectrum of this product gave the parent ion of $Y(HBpz_3)_3$, an ion for the parent amine, and did not indicate the presence of THF. A ^1H NMR spectrum in C_6D_6 indicated the presence of the parent amine. Additional, weak, poorly resolved resonances were also apparent from $\delta 7.2$-8.2.

A similar pattern was followed in the other reactions noted in Chapter V between the Grignard or organolithio reagents and the hydrotris(pyrazol-1-yl)borato(chloro) complexes. Though the reaction appeared to proceed, evidenced by the dissolution of the starting lanthanide complex, products could not be crystallized and evaporation of the solvent followed by mass and ^{1}H NMR spectral investigations gave no indication that the desired complex had been formed.

5. Synthesis of $Pr(N^ipr_2)_3 \cdot THF$

To a rapidly stirred slurry of $PrCl_3$ (5.2 g, 0.021 mol) in 10 ml of hexane was added 65 ml of THF producing a light green solution in contact with undissolved $PrCl_3$. To this $PrCl_3$ slurry was added, dropwise, 40 ml of THF solution of LiN^ipr_2 (6.6 g, 0.062 mol) at room temperature. While stirring at room temperature the color of the solution gradually changed from green to brown. After stirring overnight, the solvent was removed *in vacuo* leaving a brown solid. The residue was extracted with 100 ml of pentane and LiCl was removed by filtration. Cooling at -20°C for 18 hours produced light yellow to yellow-green crystals and a brown film coating the bottom of the flask. The crystals were separated from the supernatant liquid by fitration and redissolved in 40 ml of pentane. All but a small fraction of the crystalline material redissolved. After filtration, the clear solution was cooled at -20°C again producing light yellow crystals in contact with a brown film. Continued crystallizations from pentane produce more brown film with each operation, and lead to browner products which eventually are no longer crystalline. The yellow-green crystals which were formed initially, and which are known to represent the purest form of the compound, have been used for physical measurements. Major metal containing ions in the mass spectrum were observed for: $Pr(N^{i}pr_2)_3^+$, $Pr(N^{i}pr_2)_2^+$ and $Pr(N^{i}pr_2)^+$; other ions were observed for $HN^{i}pr_2^+$ and $C_4H_8O^+$. The infrared spectrum displayed the following bands: 1352m, 1332w, 1308w, 1262vw, 1177sh, 1170vw, 1076vw, 1033w-m, 1008w, 938w, 910m, 905m, 820w, 790w, cm^{-1}. The melting point was determined in a nitrogen filled capillary. The compound underwent a change in appearance at 47-50°C, and melted at 67-69°C. Anal. Calcd for $C_{22}H_{50}N_3OPr$: C, 51.45; H, 9.81; N, 8.18. Found: C, 50.62; H, 9.45; N, 6.72. The $N^{i}pr_2$ group was estimated by acid titration of $HN^{i}pr_2$ following alkaline hydrolysis and distillation.[134b] Calcd: 58.5; found: 56.

Preparations of the Nd and Sm analogues were carried out in a similar fashion. The problems with isolation, as above, have been noted in Chapter VI.

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